

POLYTECHNIQUE MONTRÉAL

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**Patterned Flexible and Transparent Electrodes for Future Dynamic Thin Film
Optical Devices**

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RÉSUMÉ

L'industrie de l'optoélectronique, étant en constante évolution, est toujours à l'affût de solutions innovantes pouvant améliorer les technologies existantes ou en développer de nouvelles. Les électrodes transparentes, au cœur de plusieurs produits, ne font pas exception à la règle. Parmi les défis, la conception d'électrodes, non pas seulement transparentes, mais également flexibles, marque un point d'intérêt pour l'industrie. Les oxydes transparents et conducteurs sont régulièrement utilisés pour la fabrication d'électrodes transparentes, puisqu'ils conjuguent transparence et conductivité. Parmi ceux-ci, l'oxyde d'indium-étain (ITO) est le matériel le plus fréquemment utilisé. En revanche, l'ITO est fragile, entre autres lorsqu'il est placé sous contraintes mécaniques. De plus, il nécessite une étape de recuit pour améliorer ses propriétés optoélectroniques. Ces deux facteurs font de l'ITO un matériel moins intéressant quand il s'agit d'obtenir une électrode flexible en plus d'être transparente. Par conséquent, des recherches doivent être réalisées dans le but de trouver des solutions alternatives.

Pour ce faire, de multiples techniques et matériaux peuvent être combinés pour réussir à obtenir des électrodes transparentes et flexibles. La méthode proposée, dans ce projet, repose sur l'usage de motifs pour créer des zones non conductrices hautement transparentes et des régions conductrices ayant une transparence variable selon les matériaux et les épaisseurs utilisés. Cette technique permet d'améliorer la transmission totale de l'électrode et sa flexibilité, tout en assurant un certain niveau de conductivité. Le but de l'étude étant d'amener cette transmission lumineuse (T_{lum}) à 90 % ou plus tout en maintenant la résistance de surface (R_s) en deçà ou égale à $50 \Omega/\square$. En ce qui concerne les matériaux, l'étude s'est concentrée sur l'utilisation de métaux ainsi que d'ITO. Grâce aux tests effectués sur les différentes formes et grandeurs des motifs, au cours du projet, une meilleure compréhension de leurs effets sur les propriétés optoélectroniques et la flexibilité des électrodes a pu être établie. Finalement, un appareil a dû être conçu afin de mesurer la flexibilité des électrodes, le laboratoire n'ayant pas d'outils similaires à sa disposition.

Ce projet expose une approche nouvelle et alternative afin de fabriquer des électrodes transparentes et flexibles. Le premier élément clé de cette technique consiste à utiliser un empilement de trois couches minces composées d'or et d'ITO (ITO-Au-ITO), déposées sur un substrat de PET par pulvérisation cathodique magnétron. Le substrat est préalablement couvert de motifs à base de résine photosensible, produits par un processus de photolithographie. L'utilisation de motifs est

d'ailleurs le deuxième élément clé du processus de fabrication développé au cours de cette étude. La photolithographie repose sur des procédés très connus et bien documentés permettant d'obtenir des résultats reproductibles. De plus, cette technique permet de tester une multitude de motifs en employant la même méthodologie, puisqu'il suffit de changer le masque pour obtenir des motifs différents. L'empilement d'ITO-Au-ITO permet d'obtenir une bonne conductivité ainsi qu'une bonne durabilité et flexibilité grâce à la couche d'or. Les couches d'ITO garantissent, entre autres, une hausse de la transmission en réduisant la réflexion produite par l'or. Elles permettent aussi de protéger la couche d'or contre certains dommages, telles que des rayures. En plus, la couche supérieure d'ITO assure la présence d'une surface conductrice à l'électrode, pendant que la couche inférieure permet une meilleure croissance de l'or, bonifiant ainsi ces propriétés optoélectroniques. Par la suite, les motifs créés à l'aide de la photolithographie offrent une amélioration supplémentaire de la transparence de même que de la flexibilité des électrodes.

Par conséquent, en combinant un empilement d'ITO (38 nm)/Au (20 nm)/ITO (44 nm) avec un motif de lignes aléatoires, mis en place pour éviter la diffraction, sur un substrat de PET, une électrode ayant une transmission lumineuse de 85,8 % à 550 nm ainsi qu'une résistance de surface de $49 \Omega/\square$ a été élaborée. La diffusion est maintenue sous la barre du 2 % à 550 nm et l'électrode a pu atteindre un diamètre de courbure de 9 mm avant qu'une augmentation de la résistance de surface soit observée. En utilisant un substrat de PET comportant une couche anti-réflexive de MgF_2 à son endos, il fut possible d'accroître la transmission de l'électrode décrite dans ce paragraphe jusqu'à une valeur de 90 % pour sa transmission lumineuse.

ABSTRACT

The optoelectronic industry is always looking for new technological advances and solutions to follow its constant evolution. Flexible and transparent electrodes (FTEs) are central to many new-generation products and thus require continuous improvements. Transparent conductive oxides (TCOs) are popular materials for fabricating transparent electrodes, since they combine transparency and conductivity. Indium tin oxide (ITO) is the most popular material among TCOs. However, it shows limitations when it comes to flexibility as well as below-average optoelectronic properties without the use of annealing. Therefore, for the fabrication of FTEs, finding new solutions to bypass these drawbacks is imperative.

Different avenues can be explored to create highly transparent and flexible electrodes to accomplish the aforementioned challenges. Multiple techniques and materials can be combined to obtain FTEs. The project focused on the use of ITO and metals combined with patterning as a way of improving the luminous transmittance and the flexibility of the electrodes without severely compromising their sheet resistance ($T_{\text{lum}} \geq 90\%$, $R_s \leq 50 \Omega/\square$). By testing different types and sizes of patterns, the project also studied how these parameters affect the resulting optoelectronic properties and flexibility of the electrodes. Finally, a tool had to be designed to test the flexibility of the electrodes, as no such system could perform the required measurements in the laboratory.

In this project, an alternative electrode fabrication process is presented. The latter uses a tri-layer stack of gold and ITO deposited via magnetron sputtering on a resist-patterned PET substrate produced via photolithography. Photolithography was selected as the patterning technique, since it is a well-known and documented process that provides easily repeatable results. Furthermore, by simply changing the photomask, photolithography allows the testing of a wide variety of types and sizes of patterns while keeping the same methodology, saving time and allowing for comparable results for each electrode design. The ITO-gold-ITO stack leads to high conductivity, durability, and flexibility provided by the gold layer and high transparency with the addition of the ITO layers. The latter also brought the added benefits of mechanically protecting the gold layer from damages such as scratches, as well as providing the electrode with a conductive top layer. Furthermore, the bottom ITO layer acted as a good seed layer for gold, promoting an earlier percolation threshold and improved optoelectronic properties. Afterward, the transparency and flexibility of the electrodes are further enhanced with the incorporation of patterning.

Therefore, by combining an ITO (38 nm)/Au (20 nm)/ITO (44 nm) stack with a random line pattern, implemented to eliminate diffraction, on a PET substrate, it was possible to fabricate electrodes with an 85.8% transmission at 550 nm and a sheet resistance of $49 \Omega/\square$. The scattering was below 2% at 550 nm, and the electrodes could reach a diameter of curvature of 9 mm before showing any signs of resistance changes. The transmission could be further improved by using an MgF_2 anti-reflective coating on the back side of the PET substrate, bringing the luminous transmittance to 90% for the optimized sample presented above.

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbols:

A	Absorption
α	Absorption coefficient
Ψ	Amplitude ratio between p and s polarizations
θ	Angle of propagation within a film
$\bar{y}$	Colour matching function
r_p	Complex Fresnel reflection coefficient in p polarization
r_s	Complex Fresnel reflection coefficient in s polarization
$\tilde{n}$	Complex refractive index
I_A	Current
d	Diameter of curvature
m^*	Effective mass of the carrier
e	Elementary charge
k	Extinction coefficient
I	Irradiance
L	Length of the electrode
R_{lum}	Luminous reflectance
T_{lum}	Luminous transmittance
d_{min}	Minimum diameter of curvature an electrode can reach before showing signs of resistance increase
N	Carrier concentration
D	Penetration depth
ε_0	Permittivity of the free space

Δ	Phase delay between p and s polarizations
δ	Phase shift generated by a layer
ω_p	Plasma frequency
r	Radius of curvature
R	Reflection
n	Refractive index
R_Ω	Resistance
ρ	Resistivity
S	Scattering
S_T	Scattering in transmission
R_s	Sheet resistance
E	Spectrum of the light source
z	Thickness of the coating
T	Transmission
V	Voltage
λ	Wavelength
W	Width of the electrode

Abbreviations:

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AR	Anti-reflective
CA	Conductive area

CIE	International Commission on Illumination
(CM) ²	Centre de caractérisation microscopique des matériaux
CREPEC	Centre de recherche sur les systèmes polymères et composites à haute performance
CVD	Chemical vapour deposition
DC	Direct current
DMD	Dielectric-Metal-Dielectric
E-beam	Electron beam
FCSEL	Functional Coatings and Surface Engineering Laboratory
FLA	Flash lamp annealing
FTE	Flexible and transparent electrode
IMI	ITO-Metal-ITO
IR	Image reversal
LL	Load lock
LMF	Laboratoire de Micro-Fabrication
MS	Magnetron sputtering
MSE	Mean square error
NPA	Normalized patterned area
NSL	Nanosphere lithography
NW	Nanowire
<i>OF</i>	OpenFilters
OLED	Organic light emitting diode
PA	Patterned area
PET	Polyethylene terephthalate
PVD	Physical vapour deposition

QCM	Quartz crystal microbalance
<i>QF</i>	QuickField
RF	Radiofrequency
RL	Random lines
RML®	Rolling mask lithography
SEM	Scanning electron microscopy
TCO	Transparent conductive oxide
TE	Transparent electrode
UV	Ultraviolet

CHAPTER 1 INTRODUCTION

1.1 Flexible Transparent Electrodes – Interest of Developments in the Eyewear Industry

In 2023, it was estimated that over four billion people worldwide wear glasses [1]. This number is expected to increase in the coming years due to multiple factors, such as the expanding population and its aging [1]. The growth in our reliance on screens also impacts our eyes, as it aggravates the risks of developing myopia, even more so in children and teens prone to excessive screen time [2]. For those reasons and more, the eyewear industry is always looking for new technological developments to palliate ever-growing demands and requirements.

Following the trend set by other day-to-day commodities such as televisions, refrigerators, or cars, the glasses market is simultaneously looking into the development of intelligent technologies, finding innovative solutions to offer customers smarter products that will fit their vision correction needs. For example, it is possible to think of glasses, prescription or not, that could change colour from a transparent state to a coloured state, like the ones found in sunglasses. Although this already exists in the form of photochromic lenses, which change colours in reaction to UV light, it could also be obtained with electrochromic materials, which can change their optical properties upon the application of a small electric current [3]. Linking the optical properties to a current rather than UV light would be an advantage for the user, as it would offer more control over the tint of the lens. However interesting this idea might be, one still needs to find a way to apply a current to the chosen active material. That is where flexible and transparent electrodes (FTEs) come into play, as their conductive properties allow the application of the required electric current. At the same time, their transparent nature enables them to remain barely noticeable and preserve the required and expected visibility of an ophthalmic lens. Finally, the deformability part becomes essential when considering prescription lenses where the active component may be transferred onto a curved lens or even sportswear such as ski goggles, which are also nonplanar. Thus, the electrode must maintain its conductivity when subjected to bending.

The eyewear industry would not be the only one benefiting from high-performance FTEs, as they can also be found in a multitude of technologies, such as wearable electronics, medical devices,

solar panels, cell phones, electronic paper, and many more [4], [5], [6]. Each of these technologies requires different conductivity, transparency, and flexibility degrees. This can be demonstrated firsthand, as the lenses only need to be deformable, while, for example, foldable screens found in some cell phones need to be bent at a very small diameter of curvature. Some of the mentioned applications may also have constraints regarding the materials included in the electrodes, creating a need for further fine-tuning and development in that area. The wide range of potential applications suggests that the designed electrodes could be used in other projects as they are or with slight modifications, making the development of FTEs even more interesting because of their possible hidden impact on future technologies.

Even though different types of electrodes are already available on the market, adequate conductivity, transparency, durability, and flexibility are not easily achieved to meet the standards required in the eyewear industry. Indeed, the most often used material, tin-doped indium oxide (ITO), chosen for its combination of high transparency and conductivity, has the drawback of not responding well under mechanical constraints [7]. In fact, the brittleness of ITO leads to cracking and delamination, both detrimental to its conductivity, thus making it a poor candidate for the fabrication of FTEs [8]. Furthermore, to improve its transmission and conductivity, ITO is typically annealed at 300 °C or higher [9]. This represents a challenge, especially when a high-quality ITO film is required on temperature-sensitive substrates such as polymer lenses. This led to the exploration of alternative materials to improve the performance of FTEs.

Silver is one of the most promising materials, as it possesses high conductivity and flexibility due to its metallic nature and is relatively transparent at low thicknesses [10]. However, silver has one major disadvantage: its durability. Indeed, when left unprotected, silver easily corrodes, leading to defects in the electrode (visual and/or electrical) [11], [12]. Even with the use of a protective layer, issues can still arise over time in an event that, for example, the protective layer is damaged. This is even more challenging for applications such as electrochromic devices, wearable electronics, or solar cells, where environments can be harsh. Indeed, those applications are subject to additional corrosive agents, extreme humidity, large temperature variations, or constant UV exposure [13], [14], [15], which increase the chances of damage to the electrode. This issue arises as another challenge one must overcome when developing electrodes used for the eyewear industry, further justifying the need to find new approaches and other materials for high-performance FTEs.

1.2 Context of the Research

While doing my bachelor's degree in engineering physics, I attended the class "Projet 4," which allows the students to do a one-year project in collaboration with a company. Professor Ludvik Martinu gave the class, during which he talked about his laboratory: the Functional Coatings and Surface Engineering Laboratory (FCSEL). This laboratory has the particularity of having multiple industry-oriented projects in collaboration with four world-renowned companies specializing in different fields. I thought the subject of thin films was very interesting and that having the possibility of working with an industrial partner during my master's was an exciting opportunity, which is why I applied there with great enthusiasm. This led to the realization of a project in collaboration with EssilorLuxottica.

EssilorLuxottica has been a long-time partner of the FCSEL, and they have collaborated for more than 15 years. The FCSEL's expertise in material science, optics, and mechanics and its holistic approach to thin film engineering have proven very useful to the company over the years. Indeed, the FCSEL has a large variety of vacuum deposition systems, allowing for various deposition techniques to be explored in the same project. Then, the amalgam of optical and mechanical characterization tools allows for an in-house assessment of the performance of the samples produced, closing the loop and allowing the company to achieve its objectives with well-rounded final prototypes.

For EssilorLuxottica, those objectives are based on the development of smart eyewear. This new technology could bring glasses, which are known mainly as a form of vision correction, into taking more place as protective and styling accessories in daily life. Smart eyewear could also lead to new possibilities for the public, such as having only one pair of glasses for indoor and outdoor activities, augmented reality, integrated health diagnostics, etc. However, to produce these new technological advancements, research must be done to build the different parts of the glasses. To realize this, EssilorLuxottica relies on its research centres and partnerships with university laboratories like the FCSEL at Polytechnique Montréal. Therefore, they mandated the laboratory to explore different avenues to obtain a highly transparent and flexible electrode, which led to the creation of two projects: mine and Aleksandra Pająk's Ph.D. project. These projects were done in close collaboration but with different approaches so that a maximum of options could be investigated.

While the laboratory had previous experience with transparent metallic electrodes, it was the first time that the flexibility aspect was considered when designing such a product.

1.3 Objectives of the Project

The main objective of the project was to:

Explore different avenues to obtain highly transparent and flexible electrodes without significantly compromising their conductivity.

This project aimed to produce a flexible and transparent electrode that would fit the requirements imposed by EssilorLuxottica. This means that high transmission and conductivity are required. Additionally, a certain level of flexibility is also necessary, allowing the electrode to be deformed without losing its conductivity when placed on a curved lens. To achieve this, three sub-objectives were defined as follows:

1. Deposit ITO and metallic films on polymer substrates under optimal conditions and pattern them using various approaches to increase the luminous transmittance (T_{lum}) and the flexibility without severely increasing the sheet resistance (R_s) ($T_{lum} \geq 90\%$, $R_s \leq 50 \Omega/\square$).
2. Establish a link between the resulting optoelectronic performance (R_s and T_{lum}), the resulting flexibility, and the generated patterns.
3. Develop a tool to test the flexibility of the electrodes.

In addition, it would also be ideal if the scattering in transmission (S_T) could be maintained below 1% at a wavelength of 550 nm. However, this was not established as an official objective but more as a guideline. Furthermore, it was also discussed to avoid silver in the development of the electrode to ensure adequate durability, since one of the elements of the complete device produces severe corrosion in silver.

The successful completion of the project would lead to the development of patterned electrodes on polymer substrates that are highly transparent (90% or above T_{lum}), flexible (more than a continuous layer of ITO), and conductive (R_s equal or below $50 \Omega/\square$), which can be used in ophthalmic lenses or potentially in other applications, such as wearable electronics. The project would also lead to a better understanding of how patterning (type and size of the pattern) can impact the resulting

optoelectronic properties as well as the flexibility of the electrode. Finally, the project will also bring the development of a new tool into the laboratory, one that allows for the measurement of the flexibility of the electrode. This tool will also be useful for other projects, since it can be reused any time the flexibility of a conductive sample needs to be assessed.

1.4 Outline of the Thesis

The thesis is divided into six chapters. In this chapter, Chapter 1, the subject was introduced. We detailed the pertinence of FTEs in the eyewear industry, but also in other applications. This is followed by the research context and the project's main and sub-objectives. In Chapter 2, a literature review of the topic is presented. This provides an overview of the current knowledge and fabrication procedures that are present in the scientific literature to obtain FTEs. Chapter 3 discusses the overall methodology applied during the project. The photolithography procedure and the deposition methods used will be explained in detail. This chapter also presents the different characterization tools, including the lab-designed flexibility tool. The same goes for the software used for the optimization steps (optical and pattern) and the one utilized for the masks. The main results of the project are presented in Chapter 4, which is in the form of an article submitted for publication in the "ACS Applied Materials & Interfaces" Journal. The paper showcases how the methodology explained in Chapter 3 (technics and characterization tools) allowed for the development of electrodes that met the objectives of our industrial partner. Chapter 5 offers a general discussion on various aspects of the project by presenting additional results, comments and comparisons that do not appear in the article but that are still relevant to the research. Finally, Chapter 6 proposes conclusions on the project, followed by recommendations to further improve the obtained prototypes as well as their potential integration into fully functional all-solid-state electrochromic devices.

CHAPTER 2 LITERATURE REVIEW

2.1 Foreword

This chapter presents a comprehensive review of the key principles necessary for the fabrication of transparent and flexible electrodes, as well as examples of FTEs found in the literature. The first section focuses on the frequently used materials, namely ITO and different types of metals. To continue, the concept of multilayer stacks is introduced, detailing the theory behind them, common stacks found in the literature, and their advantages when used for FTEs. Since the fabrication of FTEs is not limited to as-deposited thin films, different patterning techniques, and a 3D nanostructure, i.e., nanowires, are also presented. This includes examples from articles with their corresponding optoelectronic performance. Finally, the last section sheds light on the choice behind using photolithography as the patterning technique during the present project, highlighting its main advantages.

2.2 Materials for FTEs

2.2.1 ITO

Transparent conductive oxides (TCOs) have been used for years in various applications, such as screens, solar panels, or optoelectronic devices. Their defining characteristic is their unusual combination of optical transparency and high electrical conductivity resulting from doping semiconductors with a large band gap. The particularity of having both a transparent and a conductive material comes from the fact that these properties are usually inversely proportional. As an example, one can look at metals. The high conductivity of metals comes from the large number of free electrons that can move through the film when a voltage is applied. However, those same electrons also create high reflectance in the metallic layer due to their oscillations in the presence of an electromagnetic field, such as light, and can be characterized by the plasma frequency (ω_p). Indeed, the incident light is reflected if its frequency is below ω_p [16]. The plasma frequency can be calculated via **Equation 2.1**, derived from the Drude model. This model considers the metal to be formed of an array of fixed positive ions and free electrons that can move around in the material. The equations are based on classical mechanics and the kinetic theory of

diluted gas and, therefore, assume that the only interactions between the elements are collisions. The Drude model allows us to understand the conductivity of a metal in the presence of electron scattering based on its response to an applied electrical field [17].

$$\omega_p^2 = \frac{Ne^2}{\epsilon_0 m^*}, \quad (2.1)$$

where N is the carrier concentration (electron or hole), e is the elementary charge, ϵ_0 is the permittivity of free space, and m^* is the effective mass of the carrier.

For bulk metals, since the carrier concentration is quite high, it results in a plasma frequency value in the range of 10^{14} Hz to 10^{16} Hz, which is in the visible or in the UV, respectively. The visible light, between 4×10^{14} Hz and 7×10^{14} Hz, as well as the infrared light and everything below it, will thus be partially or completely reflected [16].

As mentioned previously, TCOs are the product of doped semiconductors, and therefore, decisions need to be made regarding the chosen materials. The band gap of the semiconductor greatly impacts the transmission (T) of the sample, since only the photons with an energy lower than the band gap energy of the material will be transmitted through the film [18]. For the visible spectrum, photons must have an energy between 1.63 eV and 3.26 eV, and thus, a band gap energy above 3 eV would be ideal to maximize the amount of transmitted light in this spectral region. Materials such as In_2O_3 , ZnO , or SnO_2 are all interesting candidates but are, by themselves, non-conductive, which is why doping is necessary to use them in transparent electrodes (TEs) [16]. The doping process introduces voluntary impurities in the semiconductor to control different characteristics, such as its conductivity as well as optical and structural properties. For TEs, the goal will be oriented towards modifying the conductivity, as it is the missing key element to obtain an adequate material.

Two types of doping exist, namely n and p doping. In n-doping, the impurities added to the semiconductor have more valence electrons than the original material, resulting in charge carriers in the form of free electrons. In the case of p-doping, the added impurities have fewer valence electrons than the semiconductor, resulting in holes in the valence band, allowing the electrons in this region to move freely and thus conduct electricity [16]. For ITO and other TCOs, n-type doping is most often used, and conductivity primarily comes from oxygen deficiencies, which lead to vacancies or metal interstitials. Part of the conductivity can also come from the substitution of a semiconductor atom by a metallic one, but a specific temperature is typically required to activate

it, for example, $\sim 150^\circ\text{C}$ for tin, present in ITO. Thus, when working with flexible substrates that are usually heat-sensitive, the conduction electrons present in the TCO mostly all result from oxygen deficiencies [19].

Regarding the transmission of these doped semiconductors, it is essential to consider that the free carriers (electrons or holes) generated by the doping also have a corresponding plasma frequency. Additionally, the free carriers, present in an excited state in the material, can also lead to photon absorption, which brings the excited carrier to another unoccupied excited state in the same band, i.e., the conduction band for an electron and the valence band for a hole. This phenomenon, called carrier absorption, reduces the amount of light transmitted through the sample, as some of the photons are absorbed in the coating. **Equation 2.2** allows us to calculate the exponential decay of the irradiance (I) based on the absorption coefficient (α) (see **Equation 2.3**) and the thickness of the material (z).

$$I = I_0 \exp^{-\alpha z}, \quad (2.2)$$

$$\alpha(\lambda) = \frac{4\pi k(\lambda)}{\lambda}, \quad (2.3)$$

where I_0 is the initial irradiance, and k is the extinction coefficient of the material, i.e., the imaginary part of the complex refractive index ($\tilde{n}$) as per **Equation 2.4**.

$$\tilde{n} = n - ik, \quad (2.4)$$

In the case of doped semiconductors, the significantly lower carrier density (N) compared to metals, allows ω_p to be in the infrared rather than the ultraviolet, thus permitting a transmittance of visible light. However, this transmitted light can still be impacted by carrier absorption, since it occurs at wavelengths where $k \neq 0$, which can include wavelengths in the visible spectrum. Therefore, to maximize the transmission, one should consider the material's absorption coefficient, as it can affect the light even below the band gap. Additionally, as per **Equation 2.2**, the thickness of the coating also influences its transmission. Indeed, it can be tempting to increase the thickness to reduce the sheet resistance, but that would lead to a decrease in transmission in the cases where $\alpha \neq 0$. Thus, the thicknesses of TCOs are usually kept between 100 nm and 200 nm, as they offer the best trade-off between transmission and conductivity [16].

Among the different TCOs, tin-doped indium oxide (ITO) is the most widely used in various applications, such as touch and display screens, solar cells, smart windows, or optoelectronic devices [20]. Indium oxide has a large band gap of around 3.75 eV, making it a good candidate for transmission of the visible spectrum, as explained above [21]. To render it conducive, In_2O_3 is most often doped with tin, creating oxygen deficiencies that, in turn, generate free carriers. While indium, tin, and oxygen are always present in ITO, the exact proportions can vary depending on the desired properties of the material. Since the conductivity, and thus the optical properties as well, are dictated by oxygen deficiencies, its flow rate during its deposition is a key parameter to optimize depending on the targeted application [19], [22], [23]. It is also easily adjustable, since most deposition systems allow for the addition of reactive gases such as O_2 . While the flow rate of oxygen and other deposition parameters such as pressure or power have varying effects on the optoelectronic properties of ITO, the transmission on glass substrates is typically above 85% in the visible spectrum, while the resistivity (ρ) is kept around $2 \times 10^{-4} \Omega \cdot \text{cm}$, explaining its frequent use in TEs [16], [24].

Post-deposition annealing has also been proven to help control the structural properties of ITO, which, in turn, have an impact on T and ρ [25], [26], [27]. For example, a study by Ahmed *et al.* on post-deposition annealing in ambient air showed that the grain size of the ITO thin film increases with increasing annealing temperatures. This consecutively led to improvements in the optoelectronic properties, particularly at annealing temperatures above 300 °C, as can be seen in **Figures 2.1a** and **2.1b**, for the transmittance and resistivity, respectively [28]. Indeed, the increase in grain sizes lowers the amount of grain boundaries, which are known to increase the material's resistivity following electron scattering. Furthermore, grain boundaries also represent one of the possible sources of light scattering in a material, among others, such as pores, impurities, or surface roughness [29]. Therefore, minimizing their amount through an increase in grain size helps reduce the scattering and thus improve the overall transmission of the ITO.

These improvements can be a marked advantage when working with heat-resistant substrates. However, annealing is a limited option when working with heat-sensitive substrates, such as polymers. In those cases, optimizing the deposition conditions becomes even more crucial to maximizing the optoelectronic properties of ITO.

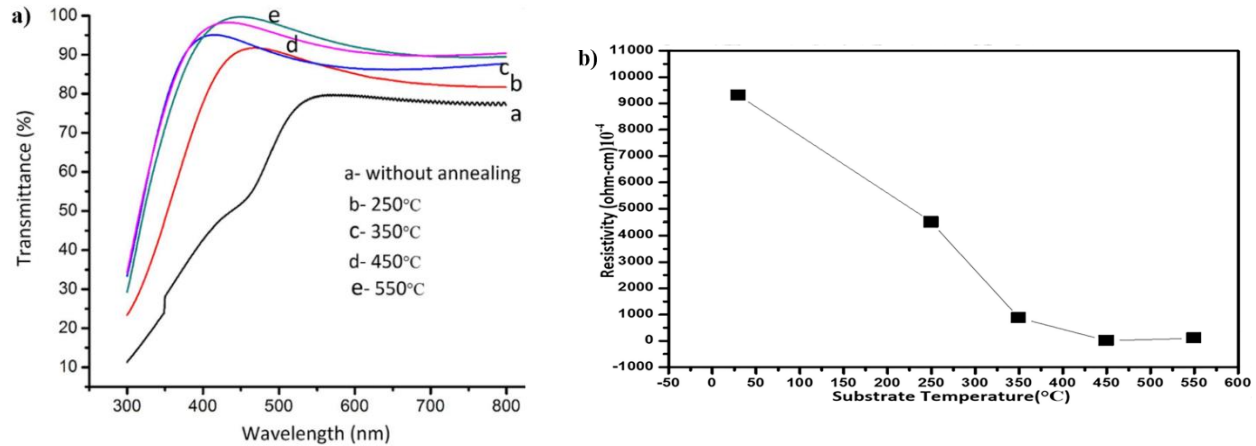


Figure 2.1: Impact of the temperature in post-deposition annealing under ambient air for ITO thin films where a) shows the effect on the transmittance and b) on the resistivity [28].

However, it is not entirely impossible to anneal materials on heat-sensitive substrates. Indeed, flash lamp annealing (FLA) allows one to anneal a sample in a very short time, i.e., on a millisecond time scale. This creates disparities in the temperature of the sample, generating a thermal non-equilibrium. Indeed, the surface (and near-surface) will be heated while deeper regions and the substrate's backside are kept at much lower temperatures [30]. Therefore, by using FLA on an ITO film, it is possible to obtain the improved optoelectronic properties brought by annealing while maintaining the substrate at a significantly lower temperature, thus permitting the use of heat-sensitive substrates.

Unfortunately, ITO has one major drawback: its flexibility. Even though this was not initially an issue for transparent electrodes, the increase in demand for flexible and transparent electrodes (FTEs) made this problem inconvenient. Indeed, ITO is very brittle, which leads to cracking and delamination when the coating is placed under mechanical solicitation [8]. Additionally, the cracks easily propagate through the film, extending the damage way beyond its starting point. This is highly detrimental to the film's conductivity and can also lead to visual defects impacting the transmission. Both these phenomena can be observed in **Figure 2.2**, realized by Zhu *et al.* as part of their study on flexible electrochromic devices [31].

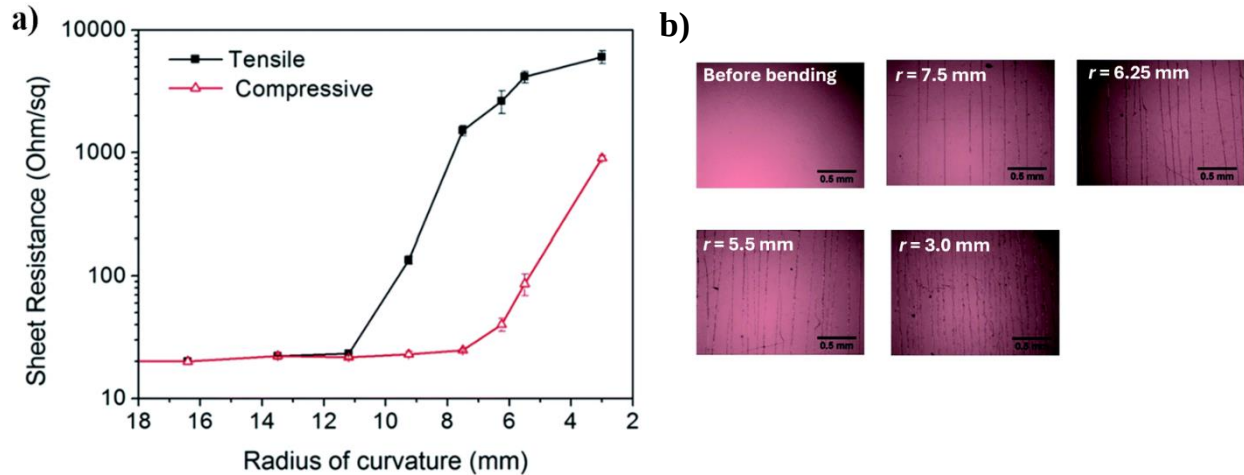


Figure 2.2: a) Sheet resistance of a sample of ITO on a PET substrate as a function of the bending radius of curvature under tensile and compressive stresses after 100 bending cycles. b) Optical microscopy images ($\times 5$ magnification) before bending and after 100 bending cycles under various radii of curvature (r) [31].

The lack of flexibility in ITO comes from its ceramic nature. Indeed, in metals, a defect, such as a crack, will generate a dislocation, as it causes an abrupt change in the arrangement of atoms. The dislocation will move as a response to the stress induced by the defect, allowing the atoms to slide past one another. This will result in the formation of slip bands, as depicted in **Figure 2.3a**, relieving the stress in the material and, for example, stopping the crack propagation [32]. However, in ceramics, the predominance of ionic bonding prevents an easy sliding of atoms. Indeed, this type of bonding creates a chain of oppositely charged ions. Thus, if an ion would like to slide past another, it would inevitably go towards an ion with the same charge as itself. Since the same charges repel each other, it would require a high quantity of energy for the complete movement of the ion to occur. Therefore, since the stress at the crack's tip cannot be relieved by the formation of slip bands, the crack will propagate through the coating, as depicted in **Figure 2.3b** [33].

The ongoing research to improve the flexibility of ITO is examining various strategies, such as reducing the thickness of the ITO, patterning the ITO film, or using nanoparticles [34], [35], [36]. Even if these various approaches are promising, alternative materials for FTEs are also being considered to respond to the industry's evolving needs.

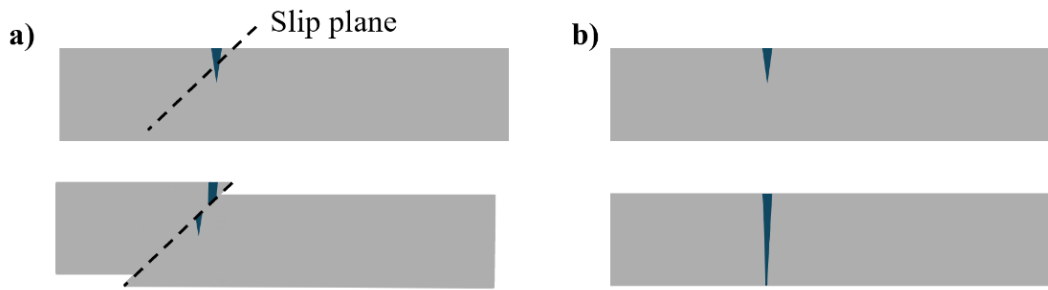


Figure 2.3: Schematics of the stress-relieving mechanism following a crack in a) metals and b) ceramics.

2.2.2 Metals

Metals have been considered among the different materials investigated as a replacement for ITO in FTEs due to their high conductivity and flexibility. Indeed, as explained above, metals have a high free carrier density that allows for excellent conductivity. Additionally, as shown in **Figure 2.3a**, the closely packed and ordered atomic arrangement in metals enables atoms to slide over each other when a force is applied or damage is formed, rendering the metal coatings flexible and ductile. Flexibility is observed when materials are bent or twisted, while ductility is related to the stretching and deformation of the materials. In both cases, the determining factor is how the material can sustain those mechanical constraints without fracturing or tearing. For FTEs, emphasis is placed on the flexibility of the coating, but both phenomena can be observed in metals.

Unfortunately, bulk metals have the disadvantage of being highly reflective. As for doped semiconductors, metals are also subject to carrier absorption. However, while the absorption coefficient is quite high for a wide range of wavelengths for bulk metals, only a small amount of light effectively penetrates the coating, leaving most of the light to be reflected as per the plasma frequency [37].

Nonetheless, it is possible to obtain a certain degree of transparency by working with metallic thin films rather than bulk materials, which is one of the techniques used to incorporate metals into FTEs. The absorption coefficient presented in **Equation 2.3** allows for the calculation of the penetration depth (D) (see **Equation 2.5**), which is a measure of how deep light can penetrate the material [38].

$$D = \frac{1}{\alpha} \quad (2.5)$$

For bulk metals, this penetration depth represents only a fraction of the total thickness of the coating, but with thin films, D gets close to or can even exceed the thickness of the coating, allowing the coating to become transparent. By using an online refraction index database and **Equation 2.3**, the penetration depth of various materials at specific wavelengths can be theoretically calculated. For example, in silver, $D = 12.2$ nm at 550 nm, while in gold, $D = 17.7$ nm at the same wavelength, where both k values were obtained from a paper by Johnson and Christy [39]. Note that more precise values can be obtained using the measured k of the deposited material rather than the one in the database.

However, thin metal films are more subjected to carrier absorption than bulk metals. In the latter, the high absorption coefficient combined with the thick coating prevents the light from reaching the bottom interface of the layer (metal/substrate interface). By having a much lower thickness, such as in thin films, the light can reach the metal/substrate interface even with the high absorption coefficient of metals. This, in turn, creates a reflection at this interface that will propagate through the coating, leading to constructive interference phenomena and, thus, additional absorption due to the increased light intensity within the film [19]. Finally, even though thin metal films can be transparent, they remain quite reflective due to the presence of free electrons, which, combined with the absorption, limits the increase in transmission that can be obtained simply by lowering the thickness of the coating [19].

In addition, a minimum thickness, which varies depending on the material, is necessary to obtain a conductive sample. Indeed, metal films deposited via physical vapour deposition (PVD) follow a Volmer-Weber growth mode, also called island growth. The films start as metallic nuclei, which develop into discontinuous islands, and as the thickness increases, the islands grow, coalesce, form a non-uniform thin film, and then ultimately form a continuous thin film [40]. For the film to start being conductive, the percolation threshold must be obtained, i.e., the lowest concentration of material at which electrical paths are formed throughout the sample. The film's conductivity further improves as it grows thicker and more continuous [41].

These limitations in transmission prompted the development of alternative solutions in which the transmission of the coating could be further improved, for example, by adding anti-reflective

layers, 3D nanostructures, or patterning [16], [19]. The most common material in FTEs is silver due to its high transparency and neutral grey colour. That being said, gold, copper, or aluminum are all candidates of interest that have also been used in research and various applications. While silver presents all the essential characteristics of a FTE, its durability can be an issue depending on the application. Indeed, silver readily corrodes when left unprotected, leading to either visual or electrical defects in the electrode, or both [11], [12]. Even when using a protective layer, issues can still arise over time, justifying the need to change the metal in the electrode depending on the application. A fine-tuning of the optoelectronic properties of the metal layers can also be done by optimizing the deposition conditions of the materials depending on the chosen deposition technique.

2.3 Multilayered Stacks

Multilayered stacks represent one of the solutions developed to increase the transmission of reflective layers, such as metallic thin films, without being detrimental to their conductivity. Various types of multilayer stacks are achievable, but one of the most used is a dielectric-metal-dielectric (DMD) stack. In this stack, dielectric layers are added on top and below the metal layer to act as anti-reflective (AR) coatings.

The anti-reflective process generates destructive interference between the light being reflected at the metal/dielectric and the dielectric/air or substrate interfaces [42]. The reflected waves must be out of phase for destructive interference to occur. The phase shift between the reflected waves is determined by the optical thickness of the layers, namely the multiplication of the layers' respective thickness and refractive index [43]. Therefore, those two parameters are crucial to obtain an efficient anti-reflective effect in the stack.

As mentioned above, in a multilayer stack, a reflection occurs at the different interfaces between the substrate, the coatings, and the medium. **Figure 2.4** shows a schematic representation of the reflections between the various interfaces in the case of a tri-layer stack. Note that while the complex refractive index is indicated in the figure, many materials will have $k = 0$, which leads to $\tilde{n} = n$ in those cases. When looking at the interface medium/dielectric (1), the resulting amplitude of the reflected wave (R_{m1}) is given by the Fresnel reflection coefficient (r_{m1}) (see **Equation 2.6**).

$$R_{m1} = r_{m1} = \frac{\tilde{n}_m \cos \theta_m - \tilde{n}_1 \cos \theta_1}{\tilde{n}_m \cos \theta_m + \tilde{n}_1 \cos \theta_1} \quad (2.6)$$

where $\tilde{n}$ is the complex refractive index (see **Equation 2.4**) of the given layer, and θ is the angle of propagation within the film.

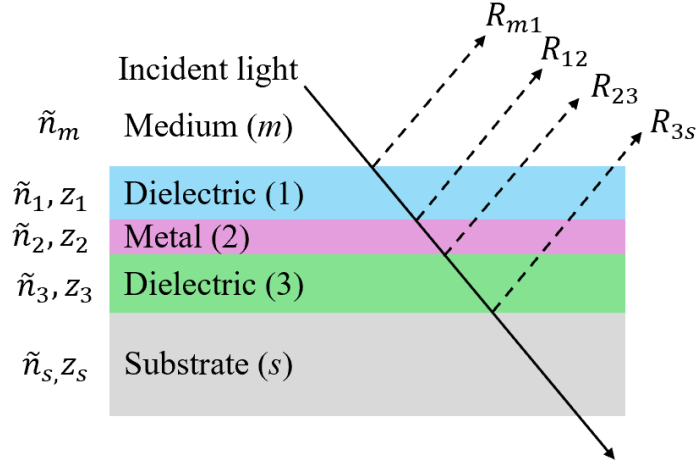


Figure 2.4: Schematic of the different reflections occurring in a tri-layer DMD stack, where z is the thickness of the material and $\tilde{n}$ is the complex refractive index.

However, the resulting total reflection, when in the presence of multiple interfaces, becomes more complicated, since the transmitted light in the different layers and the reflected light at the various interfaces also impact the final reflection. Additionally, the refractive index becomes complex in absorbing materials, adding to the many parameters already generated by the reflections at the interfaces and transmissions within the layers [43].

For understanding purposes, and to avoid getting into long equations, it is possible to look at a simplified stack where a dielectric layer (1) is placed on top of a thick metallic substrate (2) in air (m) ($n = 1$) and at normal incidence ($\theta = 0$). For this stack, the total amplitude of the reflected light will be given by **Equation 2.7**.

$$R = \frac{r_{m1} + r_{12}e^{-2i\delta_1}}{1 + r_{m1}r_{12}e^{-2i\delta_1}} \quad (2.7)$$

where r_{m1} and r_{12} are the Fresnel reflection coefficients for the respective interfaces (see **Equations 2.8** and **2.9**), and δ is the phase shift generated by a layer, where z is the thickness of the layer and λ the wavelength (see **Equation 2.10**).

$$r_{m1} = \frac{1 - \tilde{n}_1}{1 + \tilde{n}_1} \quad (2.8)$$

$$r_{12} = \frac{\tilde{n}_1 - \tilde{n}_2}{\tilde{n}_1 + \tilde{n}_2} \quad (2.9)$$

$$\delta_1 = \frac{2\pi\tilde{n}_1 z_1}{\lambda} \quad (2.10)$$

The objective of an AR coating is to produce destructive interference so that the lowest possible reflection is coming from the sample, i.e., $R = 0$. Therefore, we can put the numerator of **Equation 2.7** equal to zero, as the denominator must be non-zero. Even with the simplification of the stack and with the use of a dielectric material ($\tilde{n} = n$), the presence of the complex refractive index from the metal layer still renders the equation complicated to solve. Thus, it will not be detailed further here. However, the important aspect is that the resulting reflection depends on the refractive indices (complex or not) and thicknesses of the different layers. Therefore, the efficiency of the AR coating will rely on the optimization of those two parameters.

In the case of a DMD stack, the ideal choice of refractive index and thickness for the dielectric layers needs to be optimized depending on the type and thickness of the metal used at the centre of the stack. As it will be explained in the methodology (Section 3.6.1) and the article, software such as *OpenFilters* can be used to properly optimize the parameters of the AR layers through a transfer-matrix approach [44]. Interestingly, while the dielectric layers can be made from the same material, the stack can also be composed of different top and bottom layers. Additionally, multilayer stacking is not limited to dielectrics, as other materials can also be combined. For example, ITO can be used to create ITO-Metal-ITO (IMI) stacks. In all cases, the key to a successful stack always relies on choosing appropriate materials and thicknesses.

In FTEs, stacking can, as mentioned above, improve the overall transmission of the electrode by reducing the reflection from a highly reflective surface, such as a thin metal film. This method also has the advantage of not being detrimental to the conductivity, contrary to patterning, for example, which would improve the transmission but inevitably lower the conductivity. Depending on the material choices, stacking can also have secondary benefits. First, the dielectric layer (or ITO layers for IMI stacks) can improve the overall durability of the electrode. Indeed, these layers can mechanically protect the metal film from damage such as scratches, rendering the electrode more durable to manipulations. Additionally, encapsulating the metal film protects it from environmental

degradation, which can be a marked advantage for metals that easily corrode, such as silver [42]. By using a transparent conductive oxide in the stack, such as ITO, the presence of additional conductive layers can even help lower the resistance while having the same positive effect on the transmission of the electrode. By considering the different conductive layers as resistance placed in parallel, it is possible to obtain the total sheet resistance (R_s) a sample would have, by knowing the R_s of the individual layers. **Equation 2.11** presents an example of the calculation in the case of a tri-layer stack where all materials are conductive. Furthermore, having a conductive surface on top of the electrode can be essential in specific applications where access to electrical contacts only on the sides of the electrode is insufficient, such as in electrochromic devices.

$$\frac{1}{R_s} = \frac{1}{R_{s \text{ top}}} + \frac{1}{R_{s \text{ middle}}} + \frac{1}{R_{s \text{ bottom}}} \quad (2.11)$$

Finally, the chosen material for the bottom layer can sometimes act as a seed layer for the growth of the metal film. Depending on the seed layer, it can allow for an earlier percolation threshold during the growth of the metal film, making the coating more continuous at lower thicknesses. This can, in turn, improve the optoelectronic properties of the electrode, as one can obtain more transparent layers (from the lower thickness) with less impact on the conductivity (from the earlier percolation threshold). The seed layer can also improve wettability or reduce the surface roughness of the metal thin film. The impact of various seed layers has most commonly been studied on silver, but investigations on other materials, such as gold, have also been reported [42], [45], [46], [47], [48].

While many materials can be used to form multilayer stacks, some materials are more common than others when working with FTEs. Silver is a popular choice for the metal layer, and various materials can be utilized for the stack, such as WO_3 , ITO, ZnO, AZO, or NiO, to name a few [42], [49]. Each of these materials brings different optoelectronic properties into the stack. Gold is also a popular metal for FTEs, often combined with TiO_2 or ITO to improve its transmission [42], [50]. In all cases, it is essential to consider that parameters such as the deposition conditions, the choice of substrate, and the thickness of the films can lead to varying results in terms of optoelectronic properties, even for stacks made with the same materials. Examples of the optoelectronic properties of various stacks used for the fabrication of FTEs are presented in **Table 2.1**. This table, available in the next section, also details the optoelectronic properties of other FTEs, this time, fabricated with patterning or 3D nanostructures, allowing comparisons between the different techniques.

2.4 Patterning and 3D Nanostructures for FTEs

Patterning is a broad term that includes a multitude of techniques that allow one to shape an electrode in a 2D or 3D format. The patterns vary in shape or size and can also be placed in different arrays. Additionally, one can use 3D nanostructures for the fabrication of 3D FTEs, with nanowires being one of the most popular techniques. This section will focus on presenting the use of nanowires and various patterning methods (3D and 2D) to obtain transparent and flexible patterned electrodes. Their respective optoelectronic properties will also be compared to those of multilayered stacks. Note that the electrodes taken from the literature were designed with different objectives in mind, so the choice of materials differs depending on the desired properties of the electrode. To consider this factor while comparing the techniques, the materials, as well as a short description of the articles, are provided in addition to the general methods and optoelectronic properties.

2.4.1 3D Nanostructures - Nanowires

For FTEs, the most common way of obtaining a 3D electrode, through 3D nanostructures, is by far with nanowires (NWs). NWs are wire-shaped structures with a nanometre scale diameter and a longer variable length. Since the length is generally much larger than the width, the aspect ratio (length/width) is usually above 1000, classifying them as quasi-1D materials. In a 1D material, the electrons will interact differently than in bulk (3D) ones, thus leading to alternative electrical properties in NWs, such as proximity-induced superconductivity in non-superconductive nanowires due to quantized energy levels [51], [52]. Various types of nanowires have been developed with metals or semiconductors that fit a wide range of applications. In FTEs, metal NWs are the preferred option for their high conductivity and are often made with silver due to its neutral colour and high optical transmittance. The characteristics of the NW network largely depend on the wires' size and morphology, which varies depending on the technique used to synthesize them. Many methods are available and have been explored to synthesize NWs. A review on the synthesis of silver-based nanowires, written by Ha *et al.*, offers references to various techniques and a more thorough description of the two main ones: template-assisted synthesis and seed-based growth via polyol synthesis [53]. In summary, template-assisted synthesis uses a porous membrane to grow

the NWs alongside the pores, while polyol synthesis, for example, in the case of silver, selectively attaches Ag ions on the [111] twin plane, promoting an anisotropic growth of silver NWs [53].

The properties of the NWs can also vary according to the chosen materials, the technique used to produce the NW array as well as post-fabrication processing techniques, such as flattening the junctions [54].

Once the NWs are grown, for example, via seed-based growth, they are put into a solution that allows for an easy deposition process via spin-coating, for example. The NW network can then be combined with a multitude of techniques, such as photolithography or electrospinning, to produce FTEs with improved performance and tuned characteristics for precise applications. For example, **Figure 2.5** showcases SEM images of an electrode fabricated by Hsu *et al.* [55]. In this study, they utilized a network of silver nanowires, which are then covered with mesoscale copper wires, produced via electrospinning, to improve the transport of electrons and thus increase the conductivity of the sample [55]. The electrospinning process, explained in more detail in Section 2.4.2.1, uses polymer fibres, which can then be coated with the material of choice, i.e., copper, for the present example. The optoelectronic properties of the resulting electrode are shown in **Table 2.1**, along with the ones obtained for various NW-based transparent and flexible electrodes found in the literature.

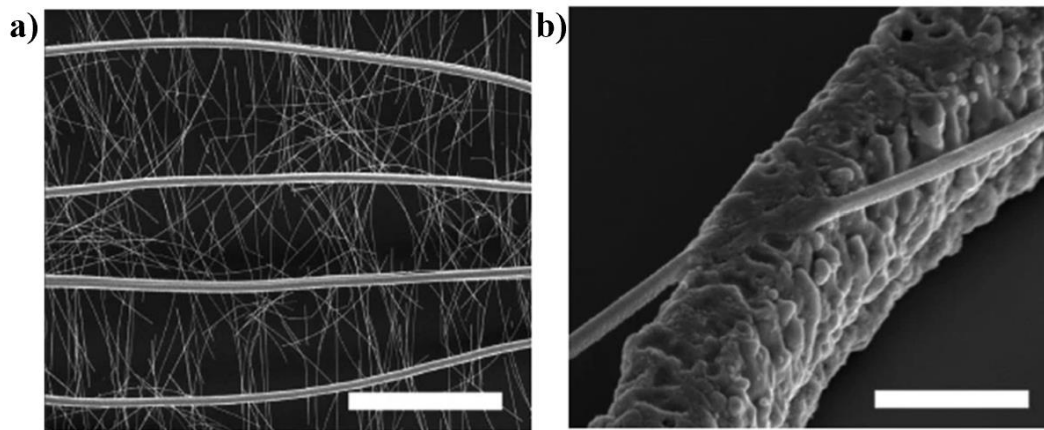


Figure 2.5: SEM images of an electrode produced by Hsu *et al.* where a) shows the horizontally aligned copper mesowires placed above the silver nanowire network (scale bar is 20 μm) and b) shows the junction between a copper and a silver wire (scale bar is 1 μm) [55].

Unfortunately, the use of NWs does come with some challenges. First, the fabrication of the NW network generates highly resistive junctions that render the sample barely conductive. Thus, post-deposition processes are often required to lower the resistivity of the junctions to obtain a conductive sample. However, most of these processes are based on heat, which is not ideal for heat-sensitive substrates [54]. Additionally, the distribution of the nanowires is also hard to control, leading to non-uniformity and varying optoelectronic properties [10]. To continue, the random stacking behaviour of the nanowires generates an increased surface roughness of the sample, which is also not ideal for the optoelectronic properties, since it increases electron and light scattering [10]. Finally, NWs have been known to have adherence problems with the substrate, which often requires surface pretreatments [10]. These elements make for a complicated multi-step process, which is not ideal for large-scale production, generating a need for alternative approaches such as patterning.

2.4.2 3D Patterning

3D patterning includes all techniques that use 3D structures to produce patterns on the substrate. These include techniques such as electrospinning and nanosphere lithography (NSL), among others.

2.4.2.1 Electrospinning

As shown with the copper mesowires presented above, electrospinning represents another method to obtain wire-like 3D structures on a substrate. Electrospinning works by using a viscoelastic polymer solution that is ejected through a nozzle under a high electric field ($\sim 1\text{--}2\text{ kV/cm}$) [56]. The initial droplet of the solution is electrified following the application of the potential difference, which results in an elongation of the droplet and a polymer jet once the voltage passes a certain threshold [57]. The polymer fibres will be collected on a grounded electrode situated at a chosen distance from the nozzle. The arrangement of the fibres can be controlled, allowing them to be completely random (as shown below in **Figure 2.6**) or well aligned (as shown above in **Figure 2.5**). The diameter of the fibres, which can vary between sub-100 nm and a few μm [55], and their morphology are affected by the applied voltage, the distance between the nozzle and the grounded

electrode as well as the flow rate and concentration of the polymer solution, which make the optimization of these parameters crucial to obtain the desired results [58].

While the technique for the electrospinning of fibres remains the same, two paths can be taken to obtain the final electrode. First, the fibres can be spun and suspended on a copper ring, which creates a free-standing network of polymer fibres. Then, this network can be coated with the chosen material, creating a nanotrough web. Next, the web is placed onto a substrate before the polymer fibres are dissolved, leaving a web-like structure made from the desired material. A schematic representation of this methodology is shown in **Figure 2.6**, which was taken from an article by Wu *et al.*, where they presented transparent electrodes based on metal nanotrough networks [59].

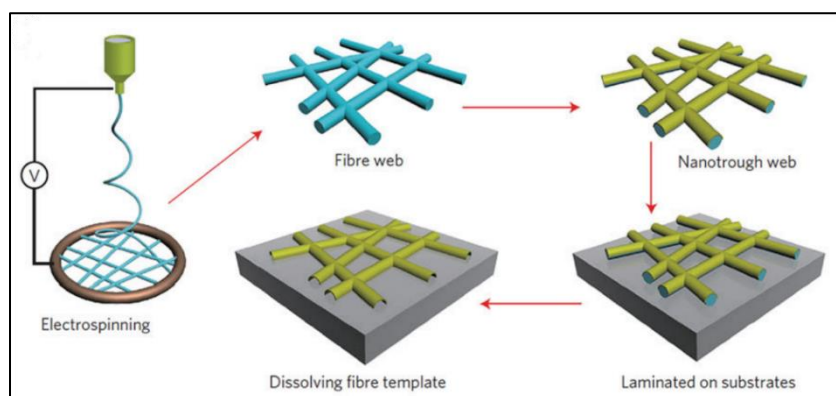


Figure 2.6: Schematic illustration of the steps for a free-standing approach in the fabrication of an electrode by electrospinning [59].

The other option is to use the fibres as a mask. For that, the fibres are first spun on a substrate previously coated with the material of choice. Then, etching (chemical or physical) removes the coating in the sections not covered by the fibres. Finally, as in the previous technique, the fibres are dissolved, which reveals the final electrode. Contrary to the first method, using the fibres as a mask allows for a final 2D pattern even though 3D structures are initially used. This was the technique used by Choi *et al.* for their development of silver electrodes for flexible organic light-emitting diodes (OLEDs) [60]. A schematic of their methodology is presented in **Figure 2.7**, and the optoelectronic properties of the electrode are presented alongside the others in **Table 2.1**. This approach removes potential issues with surface roughness and resistance increase due to the junctions between the fibres. However, in all cases, the quality of the fibres is quite sensitive to humidity, which makes repeatability difficult without a controlled environment and during the

summer months [61]. Thus, looking at alternative solutions, particularly ones that would lead to 2D patterns, can be interesting.

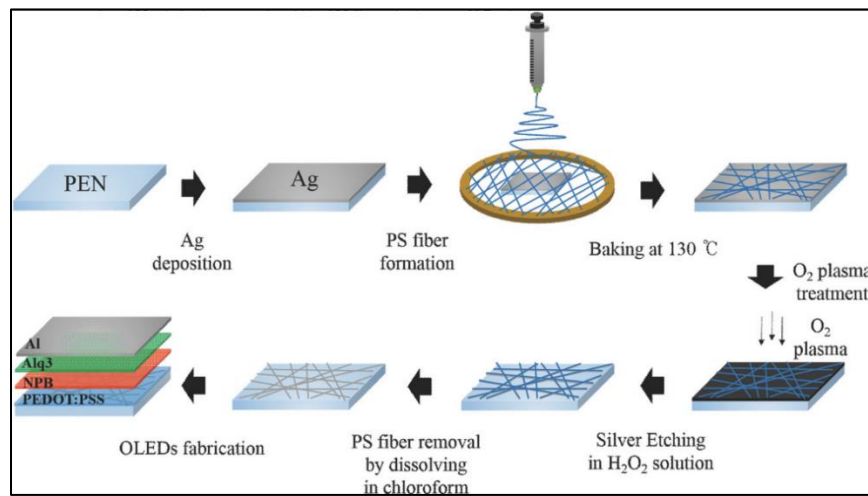


Figure 2.7: Schematic of the fabrication methodology for a silver electrode produced by electrospinning and the resulting complete OLED device [60].

2.4.2.2 Nanosphere lithography

Nanosphere lithography (NSL) is an additional technique that starts off with a 3D structure but gives a final 2D patterned electrode. NSL uses the surface tension of water to deposit, on a substrate, a monolayer of spheres, most likely made from polystyrene, in a close-packed hexagonal format [62]. Once the monolayer is achieved, the spheres can be etched to reduce their diameter and create spacing between them. The material of choice is deposited by PVD, for example, coating the exposed areas of the substrate and the spheres. The final step consists of removing the spheres, which can be achieved with sonification, resulting in a final 2D nanohole array. Schematic illustrations of the process can be found in **Figure 2.8**, taken from a study by Li *et al.*, who used NSL to produce gold nanomeshes. The optoelectronic properties of the resulting electrode are shown in **Table 2.1** [63].

NSL possesses attractive advantages, the first one being that the size of the holes in the array is easily tunable, as it depends only on the diameter of the spheres and the etching time. Additionally, combining NSL with metals creates an environment that allows for surface plasmons. With the great controllability of the structural properties of the holes, the plasmonic properties can be tuned to fit the needs of various applications, such as the precise coloration of thin films [62].

Furthermore, even though the technique uses 3D structures, the related surface roughness challenges are avoided by removing the spheres in the final product. Combined with the results obtained with electrospinning and etching, this showcases that going towards 2D electrodes helps avoid challenges brought by using 3D structures in the final device. NSL could be a good technique to produce electrodes; however, the methodology to achieve a uniform monolayer can be difficult and time-consuming, making alternative methods to obtain 2D patterned electrodes interesting to explore.

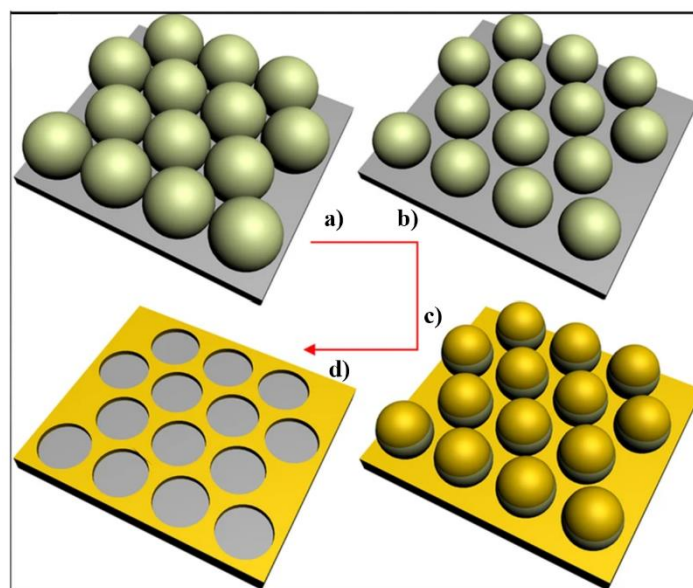


Figure 2.8: Schematic of the principal step to obtain a nanohole array from NSL where a) shows the obtained monolayer of nanospheres, b) the spheres after reactive-ion etching, c) the gold-coated sample, and d) the final nanohole array once the spheres have been removed [63].

2.4.3 2D Patterning

2D patterning regroup approaches that do not use 3D structures to obtain patterns on a sample. The most well-known technique is photolithography, but other methods, such as ink-based printing, can also be used.

2.4.3.1 Photolithography

Explained simply, photolithography uses light to transfer a pattern printed on a photomask onto a sample. For that, the sample is coated beforehand in a photosensitive resist, which sustains a

chemical change when exposed to UV light. The coating of choice can be deposited before or after the photoresist. In the first case, the resist will protect the areas of interest from etching, while in the second case, the resist will serve as a sacrificial layer to remove the unwanted parts of the coating (lift-off process). In both cases, the final step is to remove the resist to obtain the patterned electrodes. The photomask is the key element that allows for the design of the desired patterns that are then transferred onto the sample. The mask is two-toned, with sections that are opaque and sections that are left transparent. The way the mask is designed, combined with the choice of photoresist (positive or negative), will decide which areas are rendered soluble, in the case of a positive photoresist, by UV light exposure [64]. **Figure 2.9** presents schematic illustrations of the simplified methodology for both possible techniques, while using a positive photoresist.

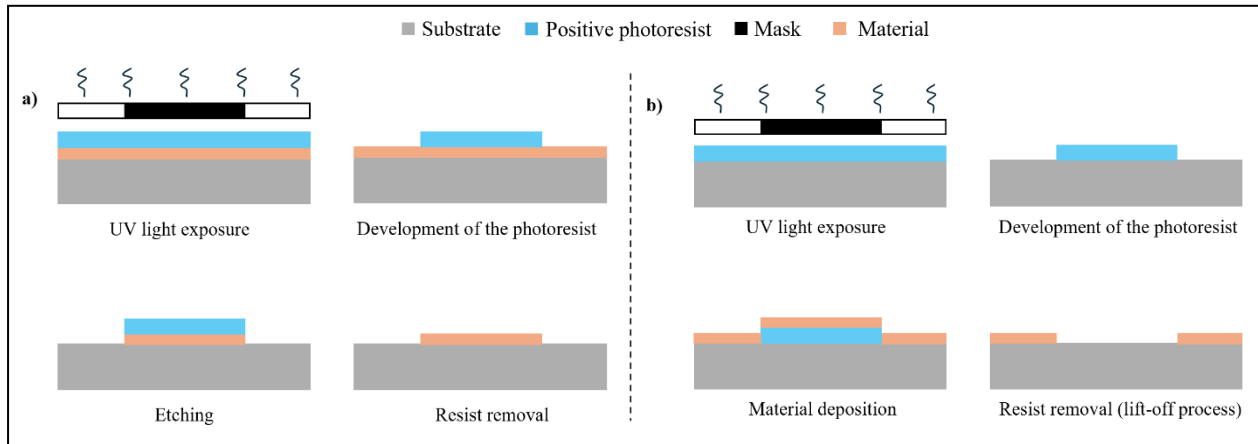


Figure 2.9: Schematic illustrations of the photolithography methodology to obtain a patterned sample by using a positive photoresist where a) the resist is used to protect the coating from etching, and b) the resist is used as a sacrificial layer and is lifted-off at the end of the process.

Photolithography is a well-known and documented process that has been used many times for various applications, including FTEs. Furthermore, this technique is renowned for giving highly uniform and repeatable results. Finally, this method also has the added benefit of being able to produce a multitude of patterns without changing the methodology, as the patterns only depend on the photomask design. However, photolithography is a relatively expensive technique due to the number of systems needed to produce the samples. Additionally, it typically requires, depending on the wanted precision, a cleanroom environment, which implies providing a contamination-free environment that maintains a low concentration of airborne particulates [65].

In FTEs, photolithography is often used to pattern electrodes with various designs and allows for the use of different materials. **Table 2.1** provides examples from the literature of the optoelectronic properties of FTEs patterned via photolithography.

2.4.3.2 Ink-Based Printing

Printing regroups a wide range of techniques that transfer a pattern onto a substrate. While many printing techniques can be used, it was decided to focus this section on ink-based printing techniques, as they are also often used in the design of FTEs. Depending on the technique, the ink can serve to trace the desired patterns, or it can also be used as a sacrificial layer to obtain areas with no coating once the ink is removed.

As an example of the first method, a study by Yang *et al.* used a silver-based ink to design a precise conductive grid of 15 μm line width on top of a substrate, as depicted in **Figure 2.10** [66]. The line width was the thinnest that could be obtained with stable printing. They used an electric field-driven microscale 3D printing technology, which creates a cone jet of the chosen material due to the potential difference between the nozzle and the substrate [66]. This differs from inkjet printing, presented in the following example, which produces material droplets [67]. In **Figure 2.10**, it is possible to see that they also applied a conductive treatment. This consisted of a sintering process at a low heating temperature of 120 °C for 30 minutes to evaporate the binder in the silver paste and allow for the silver to coalesce.

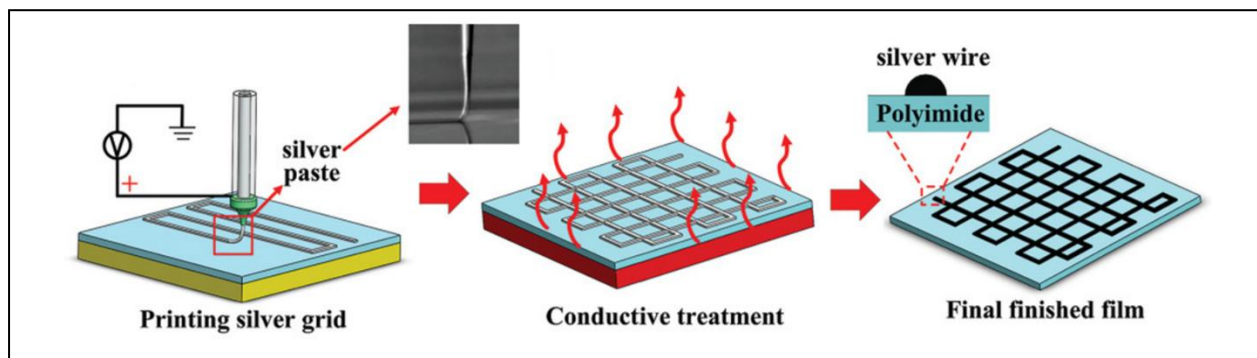


Figure 2.10: Steps to obtain a printed silver-ink-based pattern on a polyimide substrate [66].

To continue, the study by Kim *et al.* can provide an example of how ink-based printing can also be used as a sacrificial layer to produce a patterned electrode [67]. In this article, they used inkjet printing to produce a hole array, where the dots, which later created the holes, were made with

inkjet printing [67]. As mentioned above, inkjet printing produces droplets rather than a linear jet, which makes for a very efficient technique to produce uniform-sized dots between 50 μm and 100 μm in diameter [67]. The droplet size was kept the same throughout the study (67 μm), but the authors varied the type of array as well as the distance between the droplets (between 75 μm and 200 μm) [67]. **Figure 2.11** shows schematic illustrations of the steps to obtain the final patterned electrode. Similar to photolithography, the dots served as a sacrificial layer to remove the non-desired coated areas following the deposition over the substrates and the ink dots. The resulting optoelectronic properties of both this example and the previous one are presented in **Table 2.1**.

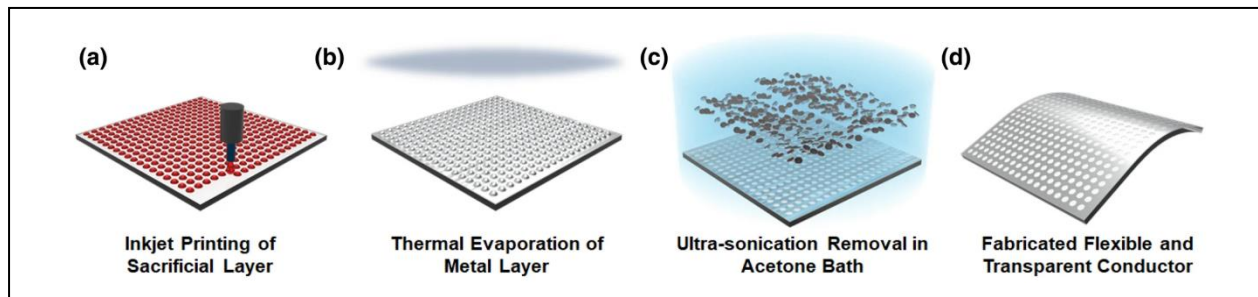


Figure 2.11: Schematic illustrations of the fabrication steps for the electrode produced via a sacrificial layer of ink dots on a flexible glass substrate where a) is the inkjet printing of the dots, b) is the coating deposition, c) is the removal of the ink dots and d) is the final patterned hole array [67].

Ink-based printing has the advantage of being more straightforward than other types of techniques, as it requires only two or three steps once the printing process is optimized. Like photolithography, it is also not restricted regarding the types of patterns it can produce, which can be advantageous depending on the application. However, obtaining a high-resolution pattern, i.e., below 15 μm or even below 50 μm depending on the printing technique, has proven to be a challenge, as it is limited by the spreading of the ink on the substrate and the need for the droplets to overlap to form continuous features (in the case of inkjet printing) [68]. The pattern size is also affected by the ink viscosity, the surface tension, and the printing conditions, all parameters that need to be optimized to maximize the resolution [67]. However, it is possible to obtain smaller line widths when using the ink as a sacrificial layer, since the wanted pattern is not produced by the ink itself, but rather by the spacing between the drawn features. Depending on the substrate and the ink used, adhesion is also a challenge that needs to be considered when tracing a desired pattern with ink-based printing.

2.4.4 Optoelectronic Properties of Various Electrodes

The previous subsections presented various methods to obtain transparent and flexible electrodes with either stacking, 3D nanostructures or patterning. Following that, it is interesting to look at how the optoelectronic properties vary depending on the technique(s) used during the fabrication of the electrodes. Thus, **Table 2.1** summarizes the optoelectronic properties of various stacked, 3D structured, or patterned electrodes. The table details the technique used as well as the material to try and obtain a more accurate comparison between the articles. That being said, the thickness of the materials, the deposition method and conditions as well as the choice of the substrate are all parameters that will affect the results. Therefore, this table serves as a short review of the available techniques and associated results rather than to conclude which approach brings about the lowest sheet resistance and highest transmission.

Table 2.1: Summary of the optoelectronic properties of transparent and flexible electrodes fabricated with various techniques and materials.

General technique	Materials	Transmission at 550 nm [%]	Sheet resistance [$\Omega/\square$]	Short description and reference
Stacked layers	Ag, WO ₃	89.5	2.85	WO ₃ (5 nm)/Ag (12 nm)/WO ₃ (105 nm)/Ag (12 nm)/WO ₃ (50 nm) stack deposited via thermal evaporation [69].
Stacked layers	Ag, ITO	~83 at 600 nm	6.0	ITO (30 nm)/Ag (10 nm)/ITO (30 nm) stack deposited via sputtering [70].
Stacked layers	Cu, ITO	~78 at 600 nm	6.0	ITO (30 nm)/Cu (16 nm)/ITO (30 nm) stack deposited via sputtering [70].
Stacked layers	Ag, ZNO	91.0	20.0	ZnO (50 nm)/AgO _x (8 nm)/ZnO (50 nm) stack deposited via magnetron sputtering. Note that the Ag was doped with oxygen (O/Ag = 3.4 at%) [71].

Table 2.2: Summary of the optoelectronic properties of transparent and flexible electrodes fabricated with various techniques and materials (cont'd).

Stacked layers	Ag, NiO	82.0	7.6	NiO (35 nm)/Ag (11 nm)/NiO (35 nm) stack deposited via electron beam evaporation [72].
Stacked layers	Au, TiO ₂	80.0	18.8	TiO ₂ (55 nm)/Au (8 nm)/TiO ₂ (55 nm) stack deposited via magnetron sputtering [73].
Stacked layers	Au, ITO	71.7	5.6	ITO (50 nm)/Au (10 nm)/ITO (40 nm) stack deposited via magnetron sputtering [74].
Nanowires	Ag	93.6	29.3	Silver NWs combined with photolithography to pattern the electrode [10].
Nanowires	Ag	83.0	30.0	Longer NWs, making a lower concentration achievable [75].
Nanowires	Ag	86.0	30.0	NWs on a crosslinked polyacrylate substrate (the NWs were overcoated and peeled off the original glass substrate) [76].
Nanowires	Au	92.0	130	NWs are drop-cast on water to promote a self-assembled mesh structure at the air-water interface [77].
Nanowires – thinner mesh	Au	92.0	227	AuNW ink is confined in a stamp to form a grid by adapting to the stamp's features. During the solvent evaporation of the ink, the wires self-assembled into dense bundles. Here, the concentration of NWs is lower, leading to a thinner mesh [78].

Table 2.3: Summary of the optoelectronic properties of transparent and flexible electrodes fabricated with various techniques and materials (cont'd).

Nanowires – thicker mesh	Au	68.0	29.0	Same method as the line above. Here, the concentration of NWs is higher, leading to a thicker mesh [78].
Nanowires	Ag, Au	84.0	24.0	A non-patterned gold layer is deposited on top of embedded silver nanowires [79].
Nano- and mesowires	Ag, Cu	92.0	0.36	A network of silver NWs is covered with equally spaced copper mesowires produced by electrospinning [55].
Electrospinning	Ag	91.8	22.3	Fibres are spun on the coated substrate, and etching removes the undesired coating [60].
Electrospinning	Cu	90.0	2.0	Free-standing electrospinning is followed by the coating of the fibres to obtain a nanotrough web [59].
Electrospinning	Au	78.0	15.0	Fibres are spun on a metal frame and transferred to the coated substrate. Then, the undesired coating is etched with Ar ions [80].
NSL – larger holes	Au	89.0	104.5	The PS spheres are etched with reactive ion etching, varying their size. Here, the holes are larger, leading to higher transmission [63].
NSL – smaller holes	Au	65.0	16.5	Same method as the line above. Here, the holes are smaller, leading to lower transmission [63].

Table 2.4: Summary of the optoelectronic properties of transparent and flexible electrodes fabricated with various techniques and materials (cont'd).

Photolithography	Ag	83.1	9.8	Hierarchical metal grids, i.e., large squares and smaller conductive diagonal lines inside the squares [7].
Photolithography	Cu, Ni	77.0	6.5	Cu square grid with a non-patterned Ni layer on top [81].
Photolithography	Cu, Al-doped ZnO	90.7	6.2	Cu hexagonal grid with a non-patterned Al-doped ZnO layer on top [82].
Photolithography	Ti, Pt	76.0	69.1	Asymmetric pentagonal metal mesh [83].
Photolithography	Au	80.0	18.0	Patterned gold square grid with a non-patterned layer of hydrogen-reduced graphene oxide on top [84].
Ink-based printing	Ag	92.3	4.82	Field-driven microscale 3D printing of a square grid with Ag ink [66].
Ink-based printing	Al	81.1	13	Sacrificial ink dots to obtain a patterned triangular hole array [67].
Rolling mask lithography (PET substrate)	Ag	96.0	5.0	NANOWEB® electrode produced by META® by combining RML® with a lift-off process (see Section 2.5 for more details) [85].
Rolling mask lithography (Glass substrate)	Al	96.0	3.5	NANOWEB® electrode produced by META® by combining RML® with etching (see Section 2.5 for more details) [85].

2.5 Choice of the Patterning Technique for the Project

After looking at multiple techniques to produce patterned electrodes, it was decided to select photolithography as the patterning technique for the project. The fact that this technique is well known and thoroughly documented played to its advantage, as it would avoid a long optimization of the parameters needed to produce the desired patterns. To continue, one of the project's goals was to test various patterns to see how their shape and size would affect the optoelectronic properties of the electrode. Photolithography is a great candidate for that purpose, as the mask design can be easily changed, while the rest of the methodology remains the same. Furthermore, the fact that the patterns are uniform, and the results are easily repeatable, allows for an accurate comparison between the different samples and patterns. Additionally, this technique leads to a 2D pattern, which, as demonstrated above, avoids challenges such as surface roughness and highly resistive junctions. Finally, all the necessary equipment was available in the cleanrooms of the Laboratoire de Micro-Fabrication at Polytechnique Montréal.

As mentioned above, the main limitation of this method is its relatively high cost, also related to the need of using a cleanroom environment. While the initial expenses cannot be avoided, an automated photolithography system would allow for an efficient fabrication of the electrodes, leading to rapid profits and thus offsetting the equipment costs. As an example, META® developed a rolling mask lithography (RML®) setup, which combines phase-shift lithography, soft lithography, and roll-to-roll patterning [85]. A schematic of the RML® setup is shown in **Figure 2.12**. META® is currently using this technique for industrial production of their flexible and transparent electrode called NANOWEB®. NANOWEB® is a square grid with fine 500 nm lines and 30 µm squares [85]. The RML® is compatible with a lift-off or an etching process as well as being achievable on both glass and PET substrates. The optoelectronic properties of one sample fabricated with each technique are shown above in **Table 2.1**.

Additionally, even if another technique is used to produce the electrodes, the results obtained in this project will remain valid. Indeed, if the other parameters stay the same, i.e., pattern design (size and type), materials, thicknesses, and deposition conditions, the optoelectronic properties should remain similar no matter the patterning technique. Finally, the knowledge gained by testing multiple types of patterns also remains, even if the patterning method changes.

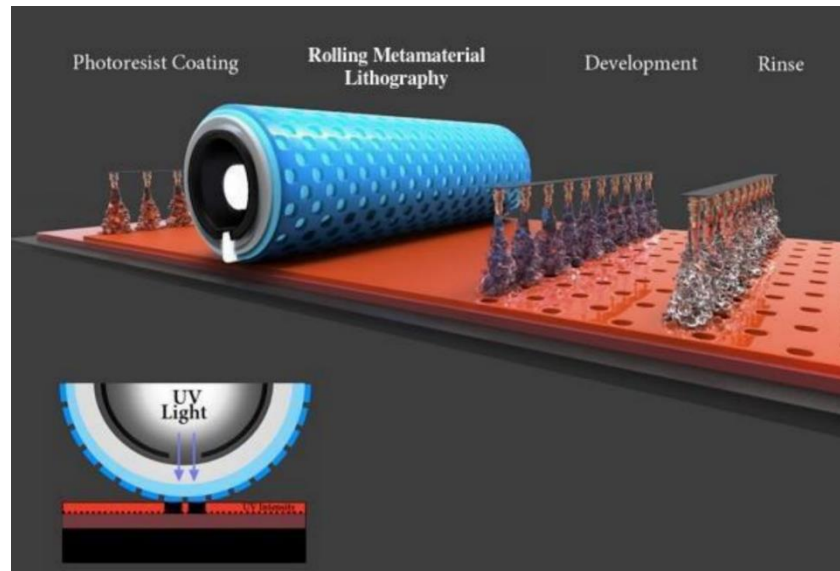


Figure 2.12: Schematic of the rolling mask lithography setup by META®, which has a 1 m by 0.3 m patterning area [85].

CHAPTER 3 METHODOLOGY

3.1 Foreword

This chapter details the systematic approach followed to pattern, deposit, characterize, and optimize the thin films and patterns used to produce highly transparent and flexible electrodes. First, the photolithography process will be described, highlighting the applied adjustments and their reasons. Then, a review of the deposition techniques and the key deposition parameters for each thin film will be given. This is followed by a description of the characterization tools, including the description of the lab-designed flexibility system, a sub-objective of this project. Finally, the optimization steps were crucial, since the electrode was built on a combination of multiple techniques that all needed to perform at their best to obtain a top-tier electrode. The two software used to optimize the thin films and the patterns are presented here, as well as the software utilized for the photomask designs.

3.2 Photolithography

Photolithography was used to create the various patterns of the electrodes. This process is divided into three essential steps: spin-coating the required photoresist, exposure to ultraviolet (UV) light, and development. To obtain a patterned electrode, the desired materials are then deposited, followed by a lift-off process. All those steps, apart from the depositions via magnetron sputtering, were conducted in cleanrooms, which consist of a controlled environment that maintains a very low concentration of airborne particulates, ideal for sensitive procedures like photolithography. The following sections and subsections will describe the methodology required for each of these steps.

3.2.1 Substrate Cleaning and Pretreatments

Two different substrates were used during the project: B270 glass and polyethylene terephthalate (PET). The B270 had the advantage of having good transmission (above 90%), a flat surface, and very well-known properties. However, for obvious reasons, it wasn't well suited for flexibility

testing. PET was thus the chosen substrate of interest when addressing the flexibility of the electrodes. However, its optical properties are more complex than the B270 (presence of scattering and anisotropy, etc.), making the two substrates complementary. It is important to note that Orma lenses were also briefly tested as a substrate, but they were disregarded following problems with the photolithography steps due to their slight curvature.

The B270 glass was cleaned in the cleanroom with a piranha solution to remove organic residues from the surface. The PET was cleaned less aggressively with only isopropanol and a gentle rub with a Kimwipe to avoid scratching the surface while still being able to remove the more tenacious stains.

Regarding pre-treatments, the B270 glass needed to be heated in an oven at 150 °C for 24 hours prior to the first photolithography step to eliminate a maximum of moisture and help improve the adherence between the resist and substrate [86]. It was thus left in the oven until a minute before the spin-coating process to minimize water absorption and allow it to cool down. For the PET, no pre-treatments were required. However, note that the PET needed to be attached to a B270 glass substrate with double-sided tape. Indeed, without a rigid base, the PET substrate would have bent and twisted during the spin-coating step at high speed. Furthermore, it was essential for the substrate to be perfectly flat during the UV exposure step to allow for an even light distribution, which was challenging for non-taped PET substrates.

3.2.2 Spin-Coating

A spin-coater can be used to uniformly deposit photoresists. A couple of drops of the chosen resist were placed at the centre of the flat substrate, and the centrifugal force produced by the high-speed rotation of the spin-coater spread the resist over the substrate [87]. The spin-coating technique is a well-known process that has been used for many years to coat substrates with resists. In this project, a spin-bake tool produced by Brewer Science (see **Figure 3.1**) was used to deposit two types of resists onto B270 and PET substrates.



Figure 3.1: Picture of the spin-bake brewer tool available in the cleanrooms of the Laboratoire de Micro-Fabrication (LMF).

The first resist deposited for the fabrication of the patterned electrodes was the LOR 5A. This resist is not photosensitive, meaning the UV light present during the exposure step will not affect it. During the development phase, the resist created a ~ 500 nm undercut below the photoresist, facilitating the lift-off process, particularly, as will be detailed shortly, following depositions by magnetron sputtering (MS) [88], [89]. The choice of this resist also came from its compatibility with the developer and lift-off products used with the imaging resist. The baking temperature of 170°C , even though slightly elevated, was still in a suitable range for the PET substrates [90]. Details of the spin-coating parameters of this resist can be found in **Table 3.1**.

The imaging resist selected for the project was the AZ5214-EIR and was used in image reversal (IR) mode, which made it act as a negative resist, providing an undercut profile following development [91], [92]. At the beginning of the project, the only resist used was the AZ5214-EIR, making the undercut profile more crucial. However, the resulting small undercut wasn't sufficient for a successful lift-off after the depositions via MS, which is why the LOR 5A was added to the methodology. The photosensitive resist also had the advantages of having low baking temperatures and being compatible with a lift-off process in an 1165 remover, a product that would not affect the PET substrates [93]. The different characteristics of the AZ5214-EIR resist can also be found in **Table 3.1**.

Table 3.1: Parameters for the resists used during the fabrication of the patterned electrodes.

Resist	Acceleration [rpm/s]	Rotation speed [rpm]	Rotation time [s]	Thickness [μm]	Soft bake [°C s]		Reversal bake [°C s]		Developer	Remover
LOR 5A	456	4000	30	~0.5	170	180	-	-	AZ726	1165
AZ5214- EIR	456	4000	30	~1.4	110	50	104	120	AZ726	1165

3.2.3 Exposure and Development

Following the spin coating of the resists, the next steps of the photolithography process are UV light exposure and the development. For that, the photomask (see Section 3.6.3) is first placed in proximity or in contact with the photoresist-covered sample. The photomask has opaque and transparent areas permitting the passage of UV light in the latter. The AZ5214-EIR resist formula includes a special crosslinking agent that becomes active, once heated, in regions that were exposed to UV light. The combination of the crosslinking agent and the exposed photoactive compound leads to an almost perfect insolubility of the exposed sections in the developer. Those sections also become no longer light-sensitive, compared to the unexposed areas, which still behave like a normal positive photoresist. To render those sections soluble, a flood exposure step (UV light with no mask for 30 seconds) is necessary following the reversal bake. During the development, the soluble areas will dissolve, leaving the samples with a negative image of the mask pattern [91].

When it comes to the sample's exposure, a calculation must be made, since the exposure time will vary depending on the photoresist's exposure dose and the UV lamp's power. This can easily be calculated via the following equation:

$$\text{Exposure time} = \frac{\text{exposure dose} \left[\frac{\text{mJ}}{\text{cm}^2} \right]}{\text{lamp power} \left[\frac{\text{mW}}{\text{cm}^2} \right]} \quad (3.1)$$

The lamp's power can be obtained before the first exposure by doing a "lamp test," which displays the current power of the lamp. The exposure dose will stay the same for a corresponding

photoresist, being at 55 mJ/cm^2 for the AZ5214-EIR, as established by the LMF personnel. As **Equation 3.1** doesn't consider the type of substrate, it can be necessary to adjust the exposure time value due to their different reflectivity. Indeed, the intensity of the reflected light that will pass through the resist a second time will differ depending on the reflectivity of the substrate. For example, when using a glass substrate, the exposure time needs to be increased by around 1.5 times to compensate for its lower reflectivity of the shortwave radiation ($\sim 10\%$) in comparison to the one of a silicon substrate ($\sim 30\%$) more commonly used in photolithography [94]. **Table 3.2** shows the mean exposure times and the corresponding development times for the different substrates. When the LOR 5A resist was added to the methodology, adjustments to the above parameters had to be made, since at least 45 seconds were necessary for sufficient undercut development. The new exposure and development times are also presented in **Table 3.2**. It can be noted that no adjustment to the exposure time was required for the PET substrate, since the additional five seconds of development didn't result in a deterioration of the patterns.

Table 3.2: Exposure and development parameters for the different substrates.

Substrate	Exposure time (no LOR 5A) [s]	Development time (no LOR 5A) [s]	Exposure time (with LOR 5A) [s]	Development time (with LOR 5A) [s]
B270 glass	10.0	30	8.5	45
PET	6.1	40	6.1	45

As in the case of spin-coating, the samples' exposure and development were conducted in the LMF's cleanrooms. An MA-6/BA-6 tool by Karl Suss, depicted in **Figure 3.2**, was used for the exposure. This tool has a 350 W mercury lamp that exposes in the UV 400, which corresponds to a wavelength range between 313 nm and 436 nm. Among the five contact modes available on the instrument, a hard contact mode was selected, since the mask and one of the substrates were made with flexible polymers. The hard contact mode ensured that the two were completely flat against one another by applying a slight external pressure. While the maximum resolution of the system is one micron, patterns were kept at a minimum size of $11 \mu\text{m}$ during this project due to limitations imposed by the mask design. Further explanations on that subject will be given in Section 3.6.3.

The samples were developed in a glass bowl with the AZ726 developer under a chemical fume hood and maintained under constant agitation to ensure an even development of the resists. This step is schematically represented in **Figure 3.7** (see Section 3.4) alongside the ones for the spin coating and exposure.



Figure 3.2: Picture of the MA-6/BA-6 tool used for the UV light exposure of the samples.

3.3 Thin Film Deposition

A large variety of vacuum deposition techniques are available to the user depending on the chosen applications, materials, or substrates. Using a vacuum deposition system has proven to be essential for increasing the mean free path of the target material's atoms and the deposition rate while limiting the material loss and contaminants brought by ambient air. Among the different vacuum deposition techniques, the most commonly used are chemical vapour deposition (CVD) and physical vapour deposition (PVD). The first one uses volatile precursors to chemically react under heating, bonding the material of interest at the surface of the substrate [95]. The latter focuses more on the evaporation or sputtering of a solid material [95]. In both cases, the results are the creation of a solid thin film at the surface of the substrate with varying stoichiometry, microstructure, and morphology depending on the chosen deposition technique and conditions [95]. The other factor that can be considered when examining those techniques is their directionality. Indeed, while PVD processes are directional techniques due to the movements of the particles from the target material

to the substrate, CDV demonstrates no directional effects, as the vapour flows around the substrate, coating every exposed area. This particularity can be a deciding element depending on the project's goals. In this work, high directionality was a key element in obtaining a successful lift-off at the end of the electrode fabrication process, thus making PVD the obvious choice. In addition, PVD is more suitable for large-scale industrial applications as well as being more environmentally friendly, since it eliminates the need for hazardous chemicals [95].

For the fabrication of the electrodes, the thin films were deposited on top of a resist-patterned substrate and lifted-off afterward, revealing the final patterned electrode. Care must be taken when choosing an appropriate PVD technique, as not all of them are equally suited for a lift-off approach. The most efficient one is known to be electron beam (e-beam) evaporation, since it is highly directional and produces films with good uniformity [96]. Therefore, this technique was selected to produce the first samples at the beginning of the project. However, following developments regarding the materials of interest, and more precisely the use of ITO, the deposition method was switched to magnetron sputtering for the second half of the project.

3.3.1 Electron Beam Evaporation

As previously mentioned, e-beam evaporation was chosen as the starting deposition technique for the fabrication of the electrodes. The samples were first placed on a substrate holder and in a chamber under vacuum. To start the process, a current is first applied to a tungsten filament to heat it. The free electrons present in the filament then acquire this thermal energy, resulting in their emission in the form of a high-intensity electron beam. With the help of a magnetic field, the electron beam is oriented towards the crucible containing the target material. The high energy of the electron beam vaporizes the target material, from which atoms can agglomerate in solid form onto the surface of the substrate, creating a thin film [95]. The deposition rate can be easily controlled via the intensity of the applied current and the thickness of the films monitored via a quartz crystal microbalance (QCM). A simplified schematic of the process is imaged in **Figure 3.3**. E-beam evaporation is also compatible with various materials, including metals and dielectrics.

The deposition process is very straightforward compared to MS, making it an efficient technique to test multiple types of materials in a short time.

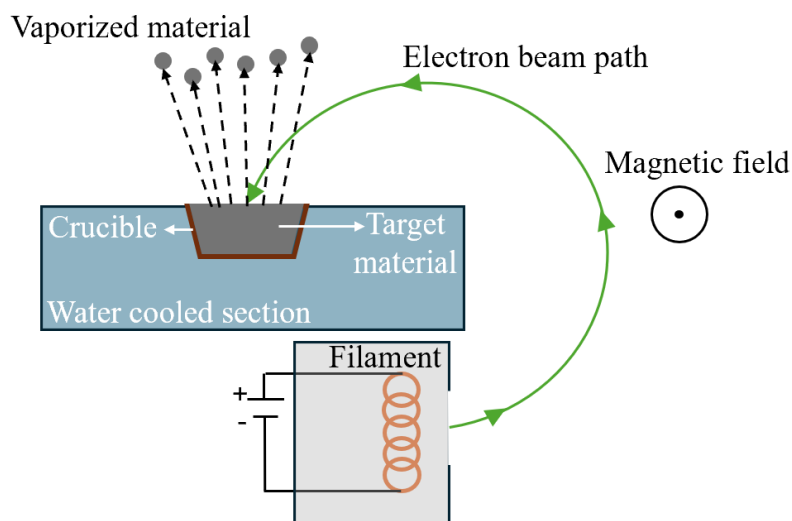
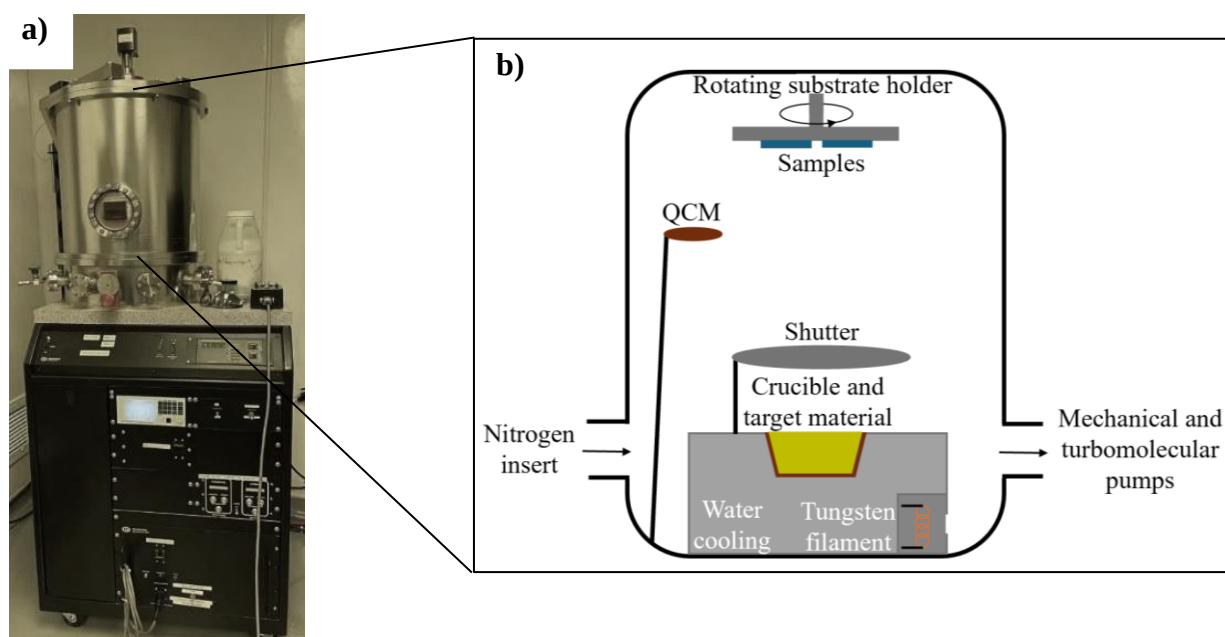


Figure 3.3: Simplified schematic of the electron beam evaporation process.

During the project, the depositions via evaporation were produced in the cleanrooms of the LMF with the electron beam system manufactured by Thermionics. The deposition rates could be varied between $1 \text{ \AA/s}$ and $10 \text{ \AA/s}$, and the base pressure was $6 \times 10^{-8} \text{ Torr}$. The substrate holder, measuring 12.7 cm in diameter, was 25.4 cm above the crucibles and target materials. A picture of the tool and schematic of the chamber can be found in **Figures 3.4a** and **3.4b**, respectively. The system was used to deposit various thin films, such as Ag, Au, Cu, and TiO_2 , to assess their optical properties and their conductivity for metals. MgF_2 thin films were also deposited with this e-beam towards the end of the project to improve the transmission of the substrates (see Section 5.4). The deposition parameters of the different materials are detailed in **Table 3.3**. The e-beam was equipped with four crucibles, allowing for the sequential deposition of materials to form, for example, a DMD stack made with TiO_2 and gold.

Table 3.3: Deposition parameters for the different materials deposited via e-beam evaporation.

Materials	Density [gm/cc]	Z-ratio	Tooling factor [%]	Deposition rate [$\text{\AA}/\text{s}$]
Ag	10.500	0.529	135	1.0
Au	19.300	0.381	135	1.0
Cu	8.930	0.437	135	1.0
MgF ₂	3.180	0.637	135	1.5
TiO ₂	4.260	0.400	158	1.5

**Figure 3.4:** a) Picture of the electron beam evaporation system available at the LMF. b) Simplified schematic representation of the deposition chamber.

As expected, the depositions made via e-beam evaporation, being highly directional, worked very well when combined with the lift-off process. The samples also had a high uniformity, even when multiple samples were being deposited simultaneously, aided by the presence of a rotating substrate holder. However, two drawbacks arose from this technique, the first one being the deposition of ITO. Indeed, the evaporated ITO had a pronounced dark colour and was completely non-

conductive. This came as no surprise, given that evaporation makes for more complex control of the stoichiometry, since indium oxide and tin oxide will evaporate at their individual vapour pressures. The other challenge came from the lack of control over the deposition parameters. Indeed, only the deposition rates could be easily controlled, leaving other parameters, such as the addition of reactive gases or ion beam assistance, unchangeable. Note that some e-beam evaporation systems, including the one available at the FCSEL, allow for more control over the deposition parameters. However, this method is still not ideal for ITO depositions, for which magnetron sputtering remains the preferred technique, as it offers more control over the stoichiometry of the material. MS also allows for the control of a wide range of deposition parameters, thus bypassing the second drawback that arose from using the e-beam system. For these reasons, it became interesting to look at MS as an alternative deposition technique for the project.

3.3.2 Magnetron Sputtering

Magnetron sputtering relies on the use of plasma to deposit high-purity materials such as metals, alloys, or ceramics. The plasma is formed when an applied voltage between the anode (substrate holder and chamber walls) and the cathode (target material) of the system accelerates free electrons of an inert gas, most commonly argon, resulting in collisions that, in turn, create more free electrons through a cascading effect, all of it leading to the ionization of the gas. In the case of MS systems, a magnetic field is also applied below the cathode, confining the plasma near the target, thus increasing the ion density and raising the sputtering rate [95]. The positive ions are attracted to the negatively charged target, thus bombarding the material with high kinetic energy and creating a momentum transfer to the atoms at the surface. This leads to two phenomena. First, if the kinetic energy is higher than the binding energy of the atoms, they will be ejected from the material's surface or, in other words, sputtered. The ejected atoms will condense on the substrate above the target, leading to the formation of a thin film. Secondly, the ion bombardment also releases secondary electrons from the target, which, in turn, will contribute to sustaining the plasma discharge [95]. **Figure 3.5** presents a schematic of the magnetron sputtering process.

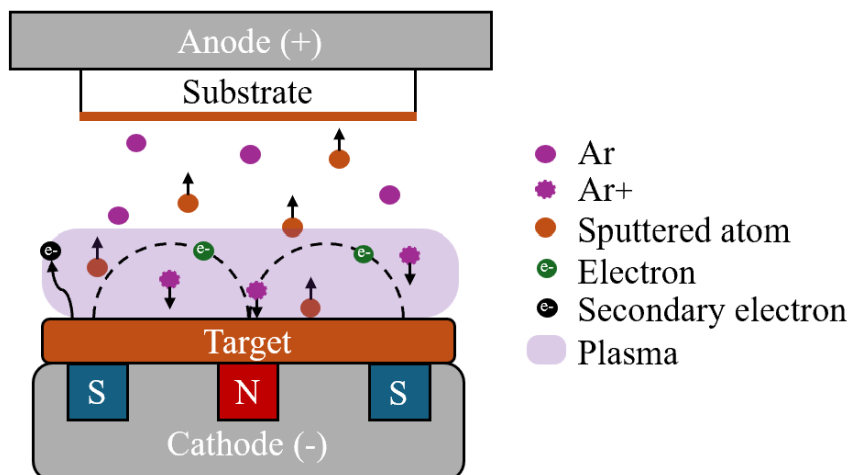


Figure 3.5: Simplified schematic of the magnetron sputtering deposition process.

For the project, a Labline 5 by Kurt J. Lesker was used to produce the thin films via magnetron sputtering. The system had two chambers, a load lock chamber (LL) and a process chamber, separated by a gate valve, allowing the samples to be inserted and removed at atmospheric pressure without breaking the vacuum in the main chamber. The process chamber is kept at a base pressure of 5×10^{-8} Torr, and the LL chamber must reach a pressure of 1.5×10^{-5} Torr or lower before the gate valve can be opened, thus maintaining a high vacuum before the depositions, ensuring less contamination. Once the correct pressure is achieved, a mechanical arm automatically transfers the samples, placed on a substrate holder, onto a rotative mount in the process chamber. The deposition system is equipped with four 3-inch magnetrons, angled at ~ 15 degrees, that allow for the sequential or simultaneous deposition of various materials without breaking the vacuum. The sequential deposition option was used to deposit the ITO/Au/ITO (IMI) stack, which are the key materials of this project, as will be explained in more detail in Chapter 4. Each magnetron possesses a shutter that prevents unwanted deposition during the target conditioning phase. The substrate holder, placed 9.6 cm above the targets, also has a shutter for added protection. A simplified schematic of the process chamber can be found in **Figure 3.6**, along with pictures of the system.

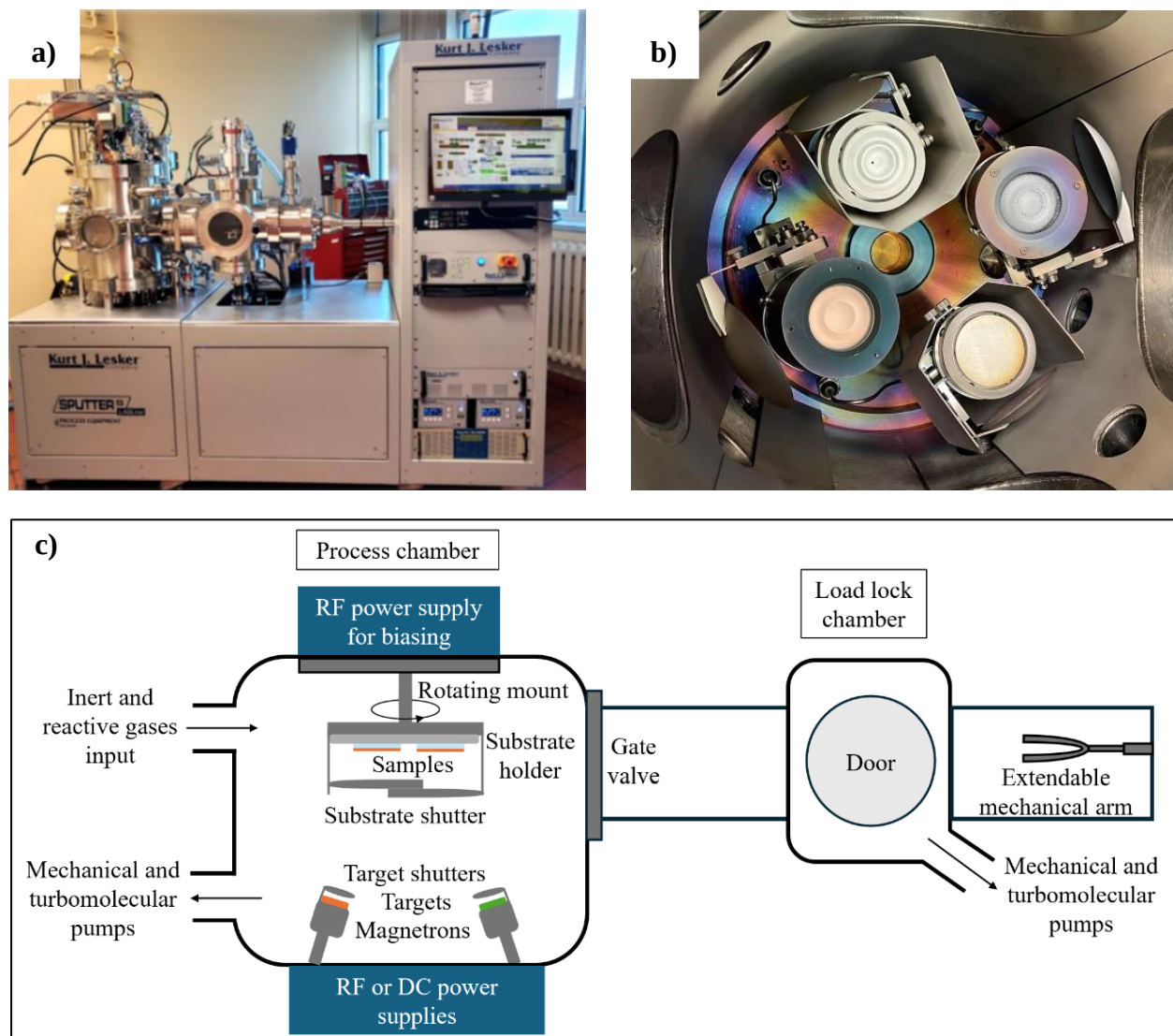


Figure 3.6: a) Picture of the Labline 5 magnetron sputtering deposition system. b) Picture of the inside of the process chamber showing the four magnetrons with their shutters open. c) Schematic representation of the inside of the process chamber and its surroundings.

The magnetrons can be run under radiofrequency (RF) or direct current (DC) modes, depending on the target material. The RF mode has the advantage of avoiding charge build-up on the target by alternating the current's electrical potential, making it more suitable for less or non-conductive materials [95]. Additionally, plasma can be maintained at a lower working gas pressure, reaching 1 mTorr [97]. This can further improve the atoms' mean free path, allowing them to reach the substrate with higher energy and, in turn, produce a more uniform and less porous film [98]. The directionality of the deposition, a key element when working with a lift-off process, can also be

improved by a lower pressure, since it reduces the number of collisions sustained by the sputtered atoms. For these reasons, the RF mode was used during the project for the deposition produced with the 99.99% pure gold target and the $\text{In}_2\text{O}_3/\text{SnO}_2$ 90/10 wt% target. For the latter, a more extensive study was done on the deposition conditions by Aleksandra Pająk as part of her Ph.D., where she varied the pressure, the power, and the addition of reactive gases, such as oxygen and hydrogen, to improve the optoelectronic properties of the resulting ITO film. With the deposition conditions presented in **Table 3.4**, she obtained a high-quality as-deposited transparent and conductive ITO ($T_{\text{lum}} = 83\%$ and $R_s = 34 \Omega/\square$ for an optically optimized thickness of 136 nm). The deposition parameters for the gold layer are also detailed in **Table 3.4**.

Table 3.4: Deposition conditions for the Au and ITO thin films. Gas concentrations are given relative to the Ar flow.

Materials	RF power density [W/cm^2]	Pressure [mTorr]	Gas flow ratio [%]	Deposition rate [nm/s]
Au	3.70	1.1	Pure Ar	0.17
ITO	3.06	2.0	Ar/O ₂ /H ₂ [100/10/20]	0.07

As mentioned previously, the system also allows for the introduction of reactive gases (H_2 , O_2 , N_2), expanding the range of possible materials as well as adding a new parameter one can work with during depositions. The reactive gas flows, the working pressure, and the power applied to the targets can all be controlled via the interface on the Labline 5. However, the deposition time needed to be monitored with a watch or a phone. To use the built-in timer of the interface, one must develop an automated recipe, which ensures a higher degree of repeatability between depositions.

Magnetron sputtering had the intended effect of solving the challenges that appeared when using e-beam evaporation. Indeed, it was possible to obtain a high-quality ITO (transparent and conductive), while also having more control over the deposition parameters of the gold films. The only downfall of MS was its compatibility with the lift-off process, which was rendered more difficult due to the angled position of the magnetrons relative to the substrate holder, resulting in the coating of the photoresist walls. However, as mentioned previously, this was solved by having

a more pronounced undercut obtained by an additional resist layer, the LOR 5A. Magnetron sputtering thus became the method of choice for the material deposition of the electrodes and is the one presented in the article.

3.4 Lift-Off Process

The last step for the fabrication of the electrodes is the lift-off process, which allows the removal of the resists and, at the same time, the non-desired coating. For that, the samples are placed in a glass bowl containing the microstrip remover under a fume hood. This step was also carried out in the cleanrooms of the LMF. Different products can be used to chemically strip the resist, such as the 1165 remover or acetone. The 1165 remover was used here, as it would not affect the PET substrate, contrary to acetone. During the stripping process, the resist is dissolved, removing the coating deposited on top of it and thus lifting it off the sample. The coating deposited directly onto the substrate will not be affected by the remover and will remain in place, creating the final structure. For the resist to be stripped, the remover must enter into contact with it, explaining the difficulties encountered when the resist walls were completely overcoated during magnetron sputtering. For the lift-off, the electrode was submerged in the 1165 remover for about 25 minutes. Agitations were made once every few minutes to ensure uniform stripping and help the structures lift off the substrate. **Figure 3.7** presents schematic illustrations of the essential steps of the electrode fabrication process, including the deposition of a tri-layer stack (DMD or IMI).

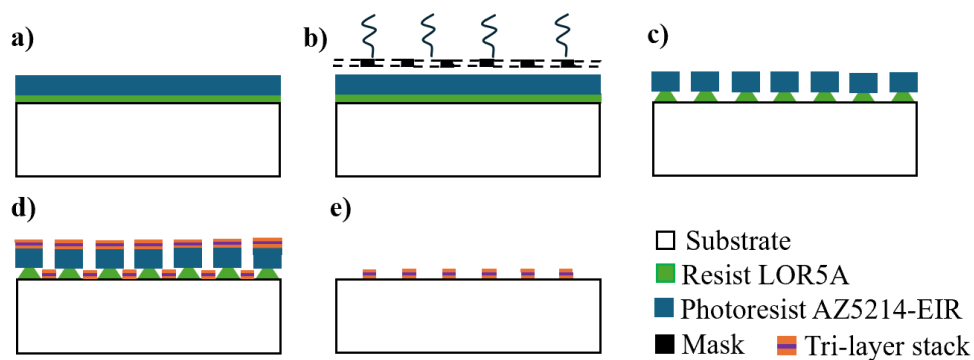


Figure 3.7: Schematic representation of the fabrication of a patterned tri-layer electrode where a) the resists are spin-coated, b) exposed to UV light, c) developed, d) the tri-layer stack is deposited and, e) the resists are lifted-off to reveal the patterned electrode.

3.5 Characterization

3.5.1 Optical

3.5.1.1 Spectrophotometry

Spectrophotometry allows for the measurement of the reflection (R), transmission (T), and scattering (S) of light as it passes through a sample. With those values, it is possible to obtain the absorption (A) of the sample with **Equation 3.2**:

$$A = 1 - R - T - S \quad (3.2)$$

In the project, the optical transmission and reflection were obtained using a Lambda 1050 spectrophotometer by Perkin Elmer. This instrument is equipped with an integrating sphere that allows for the measurements of the total reflection and transmission, which consist of both specular and scattered components. As the specular component can be removed during the measurements, the scattered components could also be obtained.

The instrument allowed for measurements between 250 nm and 2500 nm, but since the project focused on the visible spectrum, the wavelengths were usually kept between 250 nm and 800 nm. The Lambda 1050 also had the added advantage of holding the substrates completely flat for the measurements, which allowed the removal of the slight curvature of the PET substrate, eliminating a possible source of error.

In 1931, the International Commission on Illumination (CIE) established colour matching functions, which led to the creation of the xyY colour space, representing the colours according to human perception. By combining the latter with the transmittance or reflectance spectra of a sample under illumination from a known light source, it is possible to calculate the luminous transmittance (T_{lum}) and the luminous reflectance (R_{lum}) of the sample (see **Equation 3.3** and **Equation 3.4**). These parameters are often used to characterize the optical performance of FTEs, as they represent the amount of perceived transmitted or reflected light by a human observer.

$$T_{\text{lum}} = \frac{\int (T(\lambda)E(\lambda)\bar{y}(\lambda))}{\int E(\lambda)\bar{y}(\lambda)}, \quad (3.3)$$

$$R_{\text{lum}} = \frac{\int (R(\lambda)E(\lambda)\bar{y}(\lambda))}{\int E(\lambda)\bar{y}(\lambda)}, \quad (3.4)$$

where $T(\lambda)$ and $R(\lambda)$ are, respectively, the transmittance and reflectance spectra of the sample, $E(\lambda)$ is the spectrum of the light source (illuminant CIE D65 in the present case), and $\bar{y}(\lambda)$ is the colour matching function for a CIE 1931 2° standard observer.

As transparency is one of the key objectives of the project, T_{lum} will be the value that is presented rather than R_{lum} . However, it goes without saying that to obtain a high luminous transmittance, the luminous reflectance must be kept to a minimum, as per **Equation 3.2**. Furthermore, using T_{lum} compared to just T is preferable in the eyewear industry, since it serves as a more accurate representation of the client's perception.

3.5.1.2 Spectroscopic Ellipsometry

Spectroscopic ellipsometry is a simple and non-invasive technique that can provide information on many properties of the sample. During the project, this tool was used to obtain two of these properties: the optical constants (the refractive index (n) and the extinction coefficient (k)) and the thickness of the thin films.

Ellipsometry is based on the quantification of the change in polarization of a light beam following its reflection off a sample and subsequent modelling of the sample's properties. First, light passes through a polarizer and rotating compensator, resulting in a known polarization state. This polarized light then hits the sample at a given angle from which it is reflected, changing the phase and amplitude of the polarized light beam. The beam then passes through another rotating compensator and polarizer before being collected by a CCD detector. By analyzing the resulting signal, the amplitude ratio, Ψ , and phase delay, Δ , between the p and s polarizations are established from **Equation 3.5**, which defines the change in polarization. Note that since ellipsometry is an indirect method, the data must be modelled to obtain the desired film properties [99].

$$\rho = \frac{-r_p}{r_s} = \tan(\Psi)e^{i\Delta}, \quad (3.5)$$

where r_p and r_s are the complex Fresnel reflection coefficients in p and s polarization, respectively.

A RC2-XI spectroscopic ellipsometer by J.A. Woollam Co. was used combined with the *CompleteEase* software for modelling also by J.A. Woollam Co. The system allowed the measurements to be taken for a wide range of wavelengths and angles. In this work, the wavelength

range was kept between 210 nm and 2500 nm, while the measurements were performed for 10 seconds at each of the multiple angles, i.e., 45°, 55°, 65°, and 75°, which implies that Ψ and Δ were acquired as a function of wavelength as well as incidence angle.

Optical properties of single layers could be modelled using a general oscillator, which models the dielectric function of a material as a linear summation of different oscillators. The main oscillators used during the project were the following: harmonic, Drude (free electrons in conductive films), Gaussian (absorption) and Tauc-Lorentz (UV absorption), oscillators [99]. After fitting the parameters of the model to the data, it was possible to obtain information such as the surface roughness, the thickness, or the optical constants of the film. For the tri-layer stacks, the model was more complex due to the multiple layers and interactions between them, rendering the creation of an accurate model more difficult but not impossible. In that case, one would only fit the thicknesses of the layers using the optical properties obtained for single-layer samples. The mean square error (MSE), calculated by the software after each optimization, indicates the fit quality of the model. A low MSE (below 10) usually indicates an accurate fit, but one must be careful, as the model can converge towards non-physical values if the initial parameters of the model are too far from the correct ones. To help render the model more accurate, the measured R and T spectra of the samples can also be imported, helping the user select closer initial parameters.

3.5.1.3 Diffraction Test

In addition to transmission, reflection, and scattering, diffraction needs to be considered when developing FTEs for the eyewear industry. Diffraction occurs when light waves encounter obstacles or periodic structures, such as slits, resulting in the bending or spreading of the light [100]. This would be an issue for eyewear industry applications, since it would impact the vision quality of the user. A highly ordered patterned structure, such as the ones developed here, can be seen as a multitude of slits placed one after the other, thus most likely leading to diffraction depending on the size of the patterns. Indeed, for diffraction to occur, the structure needs to be comparable in size to the light's wavelength [100].

A straightforward test was conducted to determine whether the different fabricated electrodes produced diffraction patterns. A laser pointer was directed through the sample and onto a sheet of white paper placed one metre behind the sample. However, the exact value of the distance is not

crucial as long as it is significant enough to observe the diffraction pattern properly. A hole was also made in the paper to minimize the scattering produced by the strong laser light at the centre of the diffraction pattern and thus improve the visualization of the diffraction pattern in the pictures taken.

3.5.1.4 Optical Microscope and Profilometer

To help during the fabrication of the FTEs, an optical microscope was used to observe various characteristics of the patterns (size, uniformity, or shape), during the different stages of the methodology. The size could be assessed more precisely by measuring the features thanks to the software the microscope was equipped with, thus indicating if the samples were correctly exposed. Indeed, over- or under-exposure of the samples would affect the size of the features. With the mask and photoresist used in this project, an over-exposure would lead to larger lines, while an under-exposure would lead to narrower ones. Finally, during the lift-off process, the microscope could also be used to see the amount of photoresist left on the substrate and, therefore, if more time in the remover were necessary.

The optical microscope also had a purpose when it came to the flexibility of the electrodes. Indeed, the tool was used to observe the cracks formed in the presence of bent samples. Scanning electron microscopy (SEM), although used to take pictures of flat samples, could not accommodate bent ones, so another solution had to be found. For these observations, the electrode was mounted on a micrometric stage, with which the diameter of curvature could be varied. The stage was placed under the microscope and allowed for the observation, at high magnification, of the cracks formed when bending the sample.

After the development, the obtained measurements for the patterns' size could be double-checked using a profilometer, the DektakXT by Bruker. The latter allows for topographic analysis of the surface of a sample by moving a small tip laterally and measuring vertical deviations. Since the sample is patterned, it displays height variations, which can be measured to obtain the size of the features, the thickness of the photoresist, or the thickness of the deposited coatings. The latter was an advantage, particularly when depositing a multilayer stack, since obtaining its thickness via ellipsometry was nontrivial. Note that the analysis on PET substrates worked best when they were taped onto a flat surface, such as a B270 glass substrate.

3.5.2 Sheet Resistance

The sheet resistance (R_s) of the electrodes was measured using a contactless 737 conductance monitor by Delcom Instruments. The instrument uses an oscillating magnetic field created by introducing a current into the sensor's inductor coils. Then, when a conductive sample is placed in the oscillating magnetic field, it induces current loops, also known as eddy currents, in the conductive layer(s) of the sample. The power, delivered as a voltage, absorbed by the electrode is proportional to its conductivity. Thus, the software can use this value to obtain the sheet conductance and then the sheet resistance, which is displayed on the instrument or the software [101].

Using a contactless tool to measure the conductivity of the electrode was necessary due to the presence of micron-size patterns. Indeed, a probe system, also commonly used to measure the conductivity of samples, would have led to potential issues due to the size of the probes and the uncertainty of their placement during the measurement. Measuring the sheet resistance also allowed to know the resistivity of films embedded within non-conductive layers, such as in a DMD stack with gold and TiO_2 .

3.5.3 Electrode Flexibility

To assess the flexibility of the electrodes, two types of tests are usually performed in the literature. The first test focuses on the variation of the electrode's diameter of curvature (d). In contrast, the second one uses a fixed diameter but proceeds with multiple bending cycles of the sample. In both cases, the flexibility is quantified by how much the resistance varies from its initial value when submitted to mechanical constraints. With that in mind, the development of a lab-designed flexibility tool was put in motion, inspired by the different tools presented in various articles [6], [102], [103], [104].

Figure 3.8 presents a picture and a schematic of the lab-designed flexibility tool. As can be seen from the picture, the tool was built onto a pre-existing system, the Tribocorr, used for tribocorrosion measurements and developed by Tricomat Inc. The system was already equipped with a movable plate and a detector to assess the number of cycles. Both can also be controlled with front-panel commands. The Gamry Instrument software was used for the data collection and setting of the

different parameters, such as the applied voltage and the acquisition frequency. Part of the necessary wires required for the current measurement and application of the voltage were also pre-installed, leaving only the wires connected to the electrode to be added to complete the circuit. Finally, the large handle on the side of the system allowed for a variable distance between the moving and fixed plates, allowing, in the case of the electrodes, to vary the diameter of curvature.

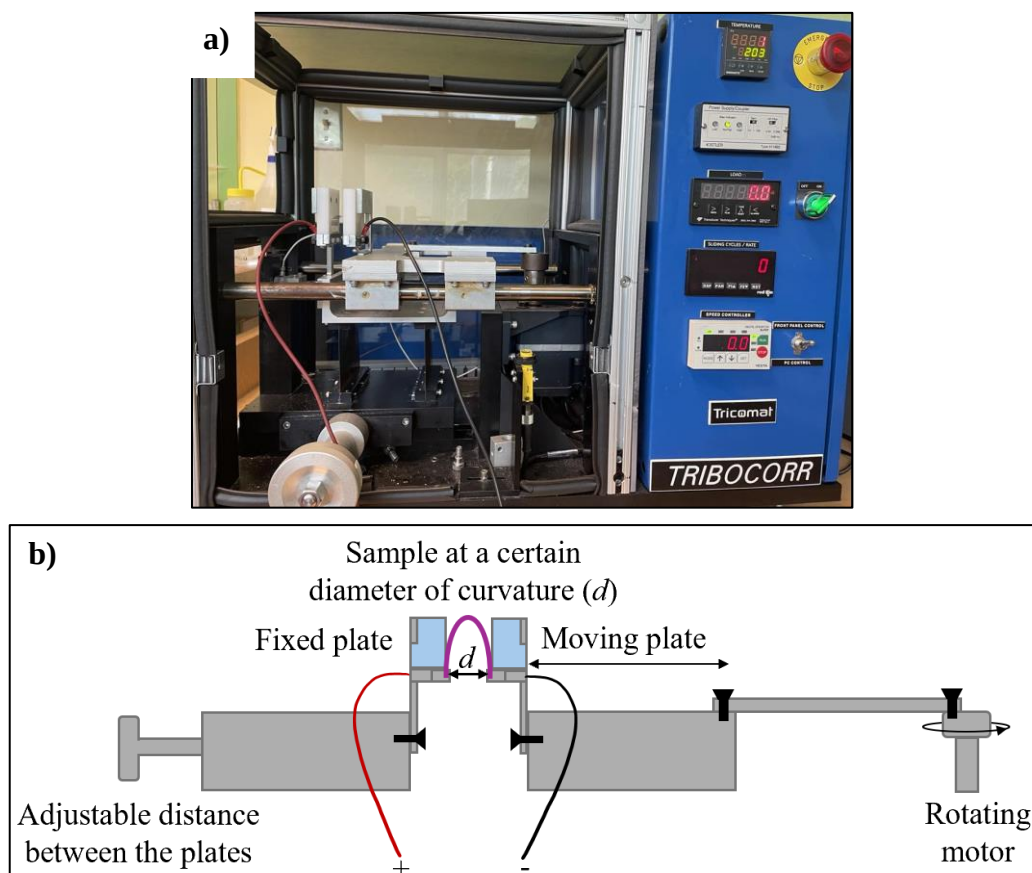


Figure 3.8: Flexibility tool system where, a) is a picture of the setup and b) is a simplified schematic with the identification of the important parts.

With most of the essential parts already on the Tribocorr, only the plates and the holders for the electrodes had to be designed from scratch. It is interesting to note that the plates were designed to fit the pre-existing system and be easily interchangeable with the tribocorrosion setup, allowing the tool to serve different purposes without compromise. The plates were designed with metallic built-in grooves, where the metal-based holders could be slid in and then screwed into place, facilitating the installation and removal of the electrodes from the system while allowing good

electrical contacts, an essential aspect, since the metallic grooves were also the connection points for the wires.

To compare the fabricated electrodes with the ones found in the literature, the same two tests as described above were performed for each electrode. In both tests, the flexibility of the coating could be measured either in tensile or compressive stress mode simply by modifying the position of the sample and placing the film facing outwards or inwards, respectively. However, since tensile stress causes more severe damage and cracking in the coating, the tests were usually performed in that position. During the tests, the instrument allowed for the application of a constant voltage at the opposing edges of the electrodes and the *in situ* measurement of the resulting current. Following the data acquisition, the resistance can easily be calculated using Ohm's law (see **Equation 3.6**), from which the sheet resistance can also be obtained with **Equation 3.7** and the dimensions of the samples, usually around 5 cm long by 1.67 cm wide. The fabricated electrodes were always approximately 5 cm by 5 cm, but they were cut into three smaller pieces for the flexibility test to be able to perform three different tests for the same sample, saving time and materials.

$$R_{\Omega} = \frac{V}{I_A}, \quad (3.6)$$

$$R_s = \frac{R_{\Omega} \cdot W}{L}, \quad (3.7)$$

where R_{Ω} is the resistance, V is the voltage, I_A is the current, which is parallel to the length of the sample, R_s is the sheet resistance, and W and L are the width and length of the sample, respectively.

During the first test, the sample is placed for tensile stress measurements and at a large diameter of curvature. Then, the diameter of curvature is manually lowered by one millimetre using the adjustment handle and a ruler. For each diameter of curvature, the current value, given in real time by the software, is noted down. Once a minimum diameter is reached, the diameter is re-increased one millimetre at a time while taking notes of the current values.

The second test focused on the flexibility of the samples when submitted to multiple bending cycles. Again, the sample is placed for a tensile stress measurement. This time, however, the diameter is fixed at a minimum d , and 1000 bending cycles are made (between d and $d + 20$ mm). A detector monitors the cycles, and the software saves the current data at a chosen acquisition

frequency. Once the cycles are completed for the set d value, the diameter was lowered by one millimetre, and the process is repeated.

A third test that could also be run was a repetition of one of the above but performed in compressive stress mode. Note that, for practical reasons, the diameter of curvature was never set lower than 7 mm, even if the system could reach 5 mm, as the PET substrate showed signs of permanent damage, i.e., creasing and plastic deformation, below this value. **Table 3.5** summarizes the key parameters for the different flexibility tests. It is important to mention that, due to the poor flexibility of ITO, a d min of 16 mm was also used during the test for multiple bending cycles when measuring a non-patterned ITO-based electrode.

Table 3.5: Summary of the parameters selected to perform the flexibility tests of the fabricated electrodes.

Type of test	d min [mm]	d max [mm]	Applied voltage [V]	Number of cycles	Oscillation frequency [Hz]	Acquisition frequency [Hz]
Minimum diameter	7	30	0.3	-	-	4
Multiple bending cycles	Between 15 and 9	d min + 20 mm	0.3	1000	1	4

3.6 Software for Optimization and Mask Design

To fabricate the flexible and transparent electrodes, optimization steps for its different components (patterns and materials) first had to be made. This subsection presents the software used to help with the optimization and the one utilized for the photomask designs. The results of the optimizations will be presented in the article found in Chapter 4.

3.6.1 Material Optimization

OpenFilters (OF) is an open-source software that allows for the design, optimization, and synthesis of optical filters [44]. The software contains a prebuilt database with the optical properties, n and

k , of different materials. However, importing measured optical properties of a material or a substrate is also possible, allowing for more precise modelling results. For the materials used in this project, i.e., gold and ITO, their optical properties were established by spectroscopic ellipsometry on a 45-nm-thick layer and a 132-nm-thick layer, respectively.

As it was explained in Chapter 2, the use of a gold layer brings interesting properties in terms of conductivity and flexibility but is also quite reflective even at low thicknesses, leading to an overall lower transmission of the sample. To improve its transparency, the concept of a DMD stack was implemented. First, by using *OF* and a custom *Python* code, both based on the transfer-matrix approach, it was possible to calculate the luminous transmittance of a DMD structure deposited on a PET substrate where the gold layer is 10 nm in thickness and where the refractive indices of the top and bottom dielectric layers and thicknesses were varied between 1.5 and 2.4, and 0 nm and 100 nm, respectively. These results made it possible to assess the refractive indices that maximized the transmission and find materials with closely corresponding n to build the stack.

The thickness of the DMD layers also has a crucial impact on the transmission of the sample. With *OF*, it was possible to input the desired materials, fix the gold thickness at a given value, and then optimize the thicknesses of the top and bottom layers to minimize the reflection, thus maximizing the transmission. This optimization step was frequently repeated, as the different thicknesses of gold, additional coatings, or a change in the substrate would generate changes in the optimum thicknesses.

3.6.2 Pattern Optimization

Once the materials were chosen, the other optimization step focused on the patterning. As detailed in Chapter 2, patterning can help improve the transmission and flexibility of the electrode but will inevitably lead to an increase in sheet resistance. That being said, optimizing the patterns' type and size makes it possible to minimize this effect. To quantify how the luminous transmittance will be affected by the aforementioned characteristics, one can simply use the following equation:

$$T_{\text{lum total}} = \text{NPA} \cdot T_{\text{lum PA}} + (1 - \text{NPA}) \cdot T_{\text{lum CA}}, \quad (3.8)$$

where NPA represents the normalized patterned area (PA), and CA is the conductive area.

However, the effect of the pattern's type and size on the conductivity is more difficult to predict. To gain better insight into the matter, the software *QuickField* (QF) was used to obtain the resulting current in terms of a fixed voltage for different types of patterns and for various sizes [105]. First, a fixed 8 cm by 8 cm simulation area was established within the software and defined as a conductive area with a chosen resistivity. Electrodes were placed at the top and bottom of the surface, where a 0.01 V potential difference was applied during the simulations. The simulations' key element was adding a non-conductive region (or PA) inside the conductive area. This PA was designed with different shapes for the various patterns of interest. Then, for each type of pattern, the simulation was run, with the size of the shape increasing in between each one. As a baseline, the simulation was also run with no patterns. With Ohm's law, the resistance could be obtained from the value of the simulation and then, with the baseline, could be normalized as an increase in the resistance. As it will be presented in Chapter 4 and Chapter 5, this optimization step led to the design of different photomasks used to pattern the electrodes.

3.6.3 Mask Design

The *KLayout* software was used to produce the designs for the different photomasks, which were then printed by the company Fineline Imaging. It is important to note that, due to their laser fabrication process on a polyester-based substrate, the resolution of the mask was limited to 8 μm , but it was even suggested to keep the smallest feature size above 10 μm to be safe. With that in mind, the lines, which are the smallest elements of the mask, were kept at a width of 11 μm .

KLayout works with a treelike structure, meaning that one pattern can be designed and then replicated a given number of times and with a chosen spacing. If the original pattern changes, the modifications will automatically propagate throughout the array, making shape and dimension variations very easy to produce. Furthermore, the patterns can be placed in different arrays, such as orthogonal or hexagonal, simply by playing with the pattern spacing and repetitions. *KLayout* also has a built-in *Python* interface, allowing users to program more complex mask designs. In the case of the project, this option was used to produce two masks: the random lines and the random squares. More details will be given on the random line mask in the article (Chapter 4) and on the random square mask in Chapter 5 (Section 5.6).

CHAPTER 4 ARTICLE 1: FABRICATION AND PERFORMANCE OF RANDOMLY PATTERNED TRI-LAYER FLEXIBLE AND TRANSPARENT ELECTRODES

4.1 Foreword

This chapter presents parts of the results obtained during the project and consists of an article submitted to “ACS Applied Materials & Interfaces” Journal. The content of the presented article represented the most promising results obtained during my Master’s project. Therefore, the conception, experimentations, simulations and data analysis were done by me. I also wrote the article, with help from the other co-authors, particularly Dr. Baloukas, in order to improve the format and content when necessary. Finally, when I had assistance regarding, for example, simulations, tool conception or SEM images, the people were credited for their involvement in the acknowledgements section.

As mentioned previously, the key elements of the project are based on the use of a tri-layer stack, made with gold and ITO, combined with patterning. Thus, the materials and patterns had to be optimized before producing the final electrodes. The first results of the article are focused on those optimizations, starting with the selection of materials for the top and bottom layers of the stack, then the optimization of the gold layer’s deposition parameters and thickness, and finishing with the optimization of the size and type of pattern. Once all the techniques were individually perfected, they were combined to produce the final electrodes, as presented in the last section of the article. The article focuses on three pattern types: small and large squares and random lines. Note that when reading the article, it is possible to see that some content was placed in a Supporting Information document. This document will not be presented directly here, but all the information can be found in Chapter 3 (for the flexibility tool) or in Chapter 5 (for the cracking and the flexibility of the non-patterned IMI stack).

4.2 Article 1: Fabrication and Performance of Randomly Patterned Tri-Layer Flexible and Transparent Electrodes

Marie-Andrée Dionne, Bill Baloukas, Oleg Zabeida, Jolanta Klemberg-Sapieha and Ludvik Martinu

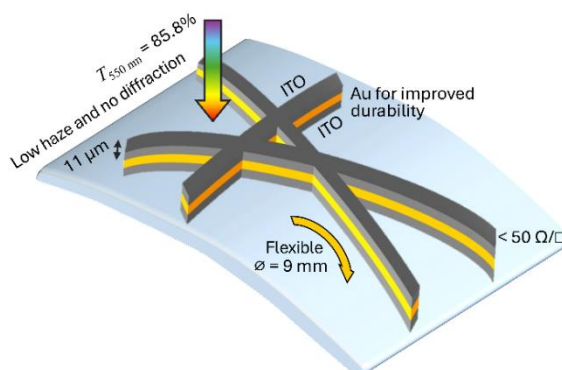
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Name of the Journal: Applied Materials & Interfaces

Date of submission: November 27, 2024

Abstract: In the fast-advancing industry of optoelectronics, transparent and flexible electrodes require continuous improvements to fit the needs of new-generation products and cutting-edge technologies. Indium tin oxide (ITO), a frequently used material for transparent electrodes, shows limitations related to flexibility and to below-average-optoelectronic properties when annealing is not possible. Thus, finding new solutions to bypass such drawbacks is imperative. To accomplish these challenges, this work presents an alternative electrode fabrication process which resides in the use of a tri-layer stack composed of gold and ITO that is deposited via magnetron sputtering on a resist-patterned PET substrate produced via photolithography. The ITO-gold-ITO stack allows for high conductivity, durability and flexibility provided by the gold layer, but also high transparency with the addition of the ITO layers. The transparency and flexibility are further improved by patterning. Specifically, by combining an ITO (38 nm)/Au (20 nm)/ITO (44 nm) stack with a random line pattern, implemented to eliminate diffraction, on a PET substrate, it was possible to fabricate electrodes with an 85.8% transmission at 550 nm and a sheet resistance of $49 \Omega/\square$. By using an MgF_2 backside-coated PET substrate, the transmission was brought up to 90.3% at 550 nm. Scattering was below 2% at 550 nm, and the electrodes could reach a diameter of curvature of 9 mm before showing any signs of changes in electrical resistance.

Keywords: Electrodes, transparent, flexible, patterned, multilayer, gold, ITO, IMI stack, random.



4.2.1 Introduction

Transparent conductive electrodes (TCEs) are a key component in various applications, such as touch screens, solar cells and optoelectronic devices [6], [106], [82]. Among all potential candidate materials, transparent conductive oxides (TCOs) and, most commonly, tin-doped indium oxide (ITO), have been primarily used due to their high transparency and conductivity [7]. However, new technological advancements now require TCEs to be flexible as well as transparent and conductive, thus requiring the development of flexible transparent electrodes (FTEs) [107]. This new characteristic is problematic in the case of ITO, as it doesn't respond well to mechanical solicitation. Indeed, the brittleness of ITO leads to cracking and delamination, both detrimental to its conductivity, thus making it a poor candidate for the fabrication of FTEs [8]. Furthermore, to improve its transmission/conductivity, ITO is typically annealed at 300 °C or higher [9]. This represents a challenge, especially when a high-quality ITO film is required on temperature-sensitive substrates. Thus, it is of interest to explore other materials and approaches to improve the performance of FTEs.

One of the most promising materials for FTEs is silver, as it possesses high conductivity and flexibility due to its metallic nature and is relatively transparent at low thicknesses [10]. To further improve its transparency, additional layers of dielectric materials can be added above and below the silver layer, leading to a multilayer stack, which can also serve as protective layers [108]. However, silver has one major drawback, namely its durability. Indeed, when left unprotected, silver readily corrodes leading to visual and/or electrical defects in the electrode [11], [12]. Even when using a protective layer, issues can arise over time if, for instance, the protective layer is damaged. This becomes an even greater issue for applications such as electrochromic devices, wearable electronics or solar cells, where the environments can be harsh, with the presence of additional corrosive agents, high humidity, large temperature variations, and long-term UV exposure [13], [14], [15]. With these applications in mind, the present study focuses on gold, a more chemically stable candidate material, to obtain a high-quality FTE.

According to the literature, novel FTEs must possess a transmission above 80% while maintaining a sheet resistance below 50 $\Omega/\square$ [7], [82], [75], [76], [84], [69], [81], [109], [83]. These performance metrics are most often sufficient in the majority of cases. However, for some specific

applications, a transmission above 90% is desired while remaining in the same sheet resistance range.

In this study, ordered and randomly patterned tri-layer transparent and flexible electrodes are fabricated on polyethylene terephthalate (PET) substrates using photolithography and magnetron sputtering. Electrodes consisting of gold encapsulated between two ITO layers, ITO-metal-ITO (IMI) stack, are proposed, and different kinds of patterns are tested. The present tri-layer architecture, inspired by the commonly used dielectric-metal-dielectric (DMD) stacks [69], [73] [110], allows for a decrease in the reflectance of the gold electrode and thus an increase in transmission without being detrimental to its conductivity. ITO also mechanically protects the gold layer from damages such as scratches, rendering the electrode more durable to manipulate in addition to the enhanced chemical stability of the gold. Patterning of the DMD stack via photolithography further improves the overall transmission and flexibility of the electrodes. To obtain the final electrodes, the experimental work was carried out in four steps, starting with the choice of encapsulating material for the DMD stack and its optimization. The second step consisted of the optimization of the deposition conditions and thickness of the conductive gold layer. In parallel, simulations were performed for various types and sizes of patterns to study their impact on the overall optoelectronic properties of the electrodes. Finally, different iterations of prototype samples were fabricated by combining the simulation results with experiments to obtain optimal final performance.

4.2.2 Experimental Methodology

4.2.2.1 Sample Deposition

Substrates used in this study were 5 cm × 5 cm squares of optically clear 127- μ m-thick PET substrates (48-5F-OC, CS Hyde Company). The depositions were carried out in a Labline 5 sputtering system (Kurt J. Lesker company), equipped with four 3-inch magnetrons in a confocal arrangement. The Au and ITO films were deposited sequentially without breaking the vacuum via radiofrequency magnetron sputtering from a 99.99% pure gold target and an In₂O₃/SnO₂ 90/10 wt% target, respectively. The precise deposition conditions for the Au and ITO are presented in **Table 4.1**.

Table 4.1: Deposition conditions for the Au and ITO thin films. Gas concentrations are given relative to the Ar flow.

Materials	RF power density [W/cm ²]	Pressure [mTorr]	Gas flow ratio [%]
Au	3.70	1.1	Pure Ar
ITO	3.06	2.0	Ar/O ₂ /H ₂ [100/10/20]

4.2.2.2 Electrode Patterning

The samples were patterned by depositing them onto a predefined photoresist and subsequent lift-off process. The essential steps of this fabrication process for tri-layer patterned electrodes are presented in **Figure 4.1**. The photoresist patterning was obtained by UV photolithography. The exposure masks were designed using the *KLayout* software and then printed by the company Fineline Imaging. Before applying the photosensitive resist, a first non-imaging resist was added as a means of generating a 500 nm undercut following its development and consequently facilitating the lift-off process after the depositions [111]. As such, LOR 5A was spin-coated at 4000 rpm for 30 seconds onto the substrate and then baked at 170 °C for 3 minutes. AZ5214-EIR photoresist used in image reversal mode was then added, also by spin-coating, at 4000 rpm for 30 seconds. This was followed by an additional baking at 110 °C for 50 s. The sample was then exposed on a MA6/BA6 mask aligner by Karl Suss for 6.1 s followed by a final baking at 104 °C for 2 minutes. The last two steps consisted of a flood exposure of 30 seconds (UV light with no mask) followed by the development of the sample for 45 seconds in an AZ726 developer [92].

It is interesting to note that the *KLayout* software, used for the mask design, has a built-in *Python* interface allowing one to program more complex mask designs. It was thus possible to write a code generating lines, with a fixed line width of 11 μm , placed at random angles and random positions inside a predefined area of 6.35 cm by 6.35 cm. The lines were simply cut if the random positions made them exceed the defined area. The number of lines was controlled via a variable in the code, and their coverage was estimated using another *Python* code outside of *KLayout*, making it easily adjustable for future iterations of the mask.

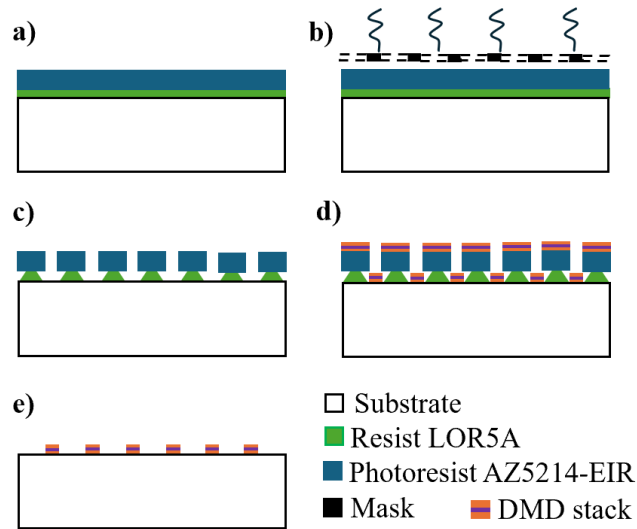


Figure 4.1: Schematic representation of the fabrication of a tri-layer patterned electrode where a) the resists are spin-coated, b) exposed to UV light, c) developed, d) the DMD stack is deposited, and e) the resists are lifted-off to reveal the patterned electrode.

4.2.2.3 Electrode Characterization

The sheet resistance (R_s) of the electrodes was measured using a contactless 737 conductance monitor by Delcom Instruments. The optical transmission and reflection were obtained using a Lambda 1050 spectrophotometer by Perkin Elmer equipped with an integrating sphere. The latter allowed for the measurements of the total reflection (R) and transmission (T), which consist of both specular and scattered components. As the specular component can be removed during the measurements, the scattered components could also be obtained. Note that, having measured the total transmission and reflection, the absorption can also be readily calculated ($A = 1 - R - T$). For reference purposes, it is worthwhile to indicate that the PET substrate alone exhibited a luminous transmittance (T_{lum}), which represents the amount of perceived transmitted light by a human observer (see **Equation 4.1**), of 88.6% with 1.2% of scattering in transmission (S_T) at 550 nm.

$$T_{lum} = \frac{\int (T(\lambda)E(\lambda)\bar{y}(\lambda))}{\int E(\lambda)\bar{y}(\lambda)}, \quad (4.1)$$

where $T(\lambda)$ is the transmittance spectrum of the sample, $E(\lambda)$ is the spectrum of the light source (illuminant CIE D65), and $\bar{y}(\lambda)$ is the colour matching function for a CIE 1931 2° standard observer.

The optical properties of the coatings and the substrates, the refractive index (n) and the extinction coefficient (k) were measured on a RC2-XI ellipsometer by J. A. Woollam Co. The same tool was also used for establishing the thickness of the films via modelling in *CompleteEase*, also from J. A. Woollam Co.

Finally, the flexibility was tested using a lab-designed tool that was inspired by the literature [6], [102], [103], [104]. This instrument allowed for the application of a constant voltage at the opposing edges of the electrodes and the *in situ* measurement of the resulting current. Once installed, the 5 cm long by 1.67 cm wide samples could be bent for a specific number of cycles using a movable motorized plate. The distance between the two sides of the electrodes, which corresponds to the diameter of curvature, could be varied from 5 mm to 40 mm. The electrode could also be placed with the coating facing outwards or inwards, for tensile or compressive stress measurements, respectively. For practical reasons, the diameter of curvature was never set to lower than 7 mm, as the PET substrate showed signs of permanent damage, i.e., creasing and plastic deformation, below this value. Photos and more details about this instrument can be found in the Supporting Information document.

4.2.3 Results and Discussion

4.2.3.1 IMI Stack Design

Metallic layers are very useful when it comes to increasing conductivity. However, even at low thicknesses, they are highly reflective; for example, a 10 nm gold layer displays a 19% luminous reflectance. This high reflectance leads to an overall lower optical transmission in the samples. One approach to improve their transparency resides in the addition of anti-reflective (AR) layers below and above the metallic film. This works by generating a destructive interference between the light being reflected at the metal/dielectric and the dielectric/air or substrate interfaces [42]. The optical thickness of the layers —the product of the refractive index and thickness— is thus critical for obtaining efficient AR properties.

These two parameters can be adjusted and optimized with a combination of the *OpenFilters* software and a custom *Python* code, also based on the transfer-matrix approach [44]. In both cases, the measured optical properties, n and k , of the materials and the substrate are entered before

modelling, where the gold layer's properties were established for a 45-nm-thick layer. It is then possible to calculate the luminous transmittance of a DMD structure deposited on a PET substrate where the gold layer is 10 nm in thickness and where the refractive indices of the top and bottom dielectric layers and thicknesses are varied between 1.5 and 2.4, and 0 nm and 100 nm, respectively. **Figure 4.2a** shows the resulting map of these calculations, produced with the *Python* code, where, for each refractive index combination, the optimal thicknesses of the dielectrics are chosen to maximize the transmission. As expected, the luminous transmittance is observed to vary depending on the refractive indices of the layers. The highest transmission values are obtained when the bottom layer has a high refractive index above 2.2 and the top layer between 1.9 and 2.0 (1.98 being optimal).

These results are very similar to what was observed in a study by Rumsby *et al.* that uses a modelling approach to optimize a silver-based tri-layer DMD stack. Indeed, for a 10 nm silver film, the lowest reflection was obtained when the refractive index of the bottom layer was 2.2, while the one for the top layer was 1.8 [112]. A more mathematical approach employed by Ji *et al.* also came to similar conclusions [43]. Considering these refractive index values, various materials with high refractive indices could be considered for the bottom layer. Regarding the top layer, the required lower refractive index allowed for an even wider range of potential candidate materials. However, aside from its refractive index, the top layer should also, ideally, be conductive, as this is critical for multiple applications. As such, we selected ITO as the top layer material. The refractive index of our ITO layer, deposited via magnetron sputtering (see **Table 4.1**), was 1.94 at 550 nm, which is close to the 1.98 optimal value for the top layer. Even though this refractive index is not above 2.2, ITO was also used for the bottom layer of the stack. This choice was supported by literature, as ITO is often used in IMI stacks in various Au- or Ag-based electrodes [74], [70]. Furthermore, preliminary tests indicated that the bottom ITO layer seemed to act as a good seed layer when considering the growth of gold, making ITO an interesting material for the bottom layer, despite a theoretical 2% trade-off in luminous transmittance. More details on the seed layer effect can be found in Section 4.2.3.2.

Figure 4.2b shows the theoretical increase in transmission obtained when using an IMI stack in comparison to a single gold layer, for the same gold thickness of 10 nm, resulting in a 14.75% increase in luminous transmittance. This specific gold thickness was chosen, as it offered low enough sheet resistance (ideally below $10 \Omega/\square$) so that the final R_s value would still be in the

targeted range when the samples were patterned. Thicker gold layers would also have had $R_s < 10 \Omega/\square$, but would have led to a lower transmission. Regarding the conductivity, both ITO layers (43 nm optimized thickness) were conductive with a sheet resistance of $\sim 150 \Omega/\square$, calculated from the ellipsometry-derived resistivity of a 132-nm-thick ITO layer. Note that the sheet resistance could be further improved by using thicker ITO layers. However, this could potentially be detrimental to the flexibility and growth of the gold film.

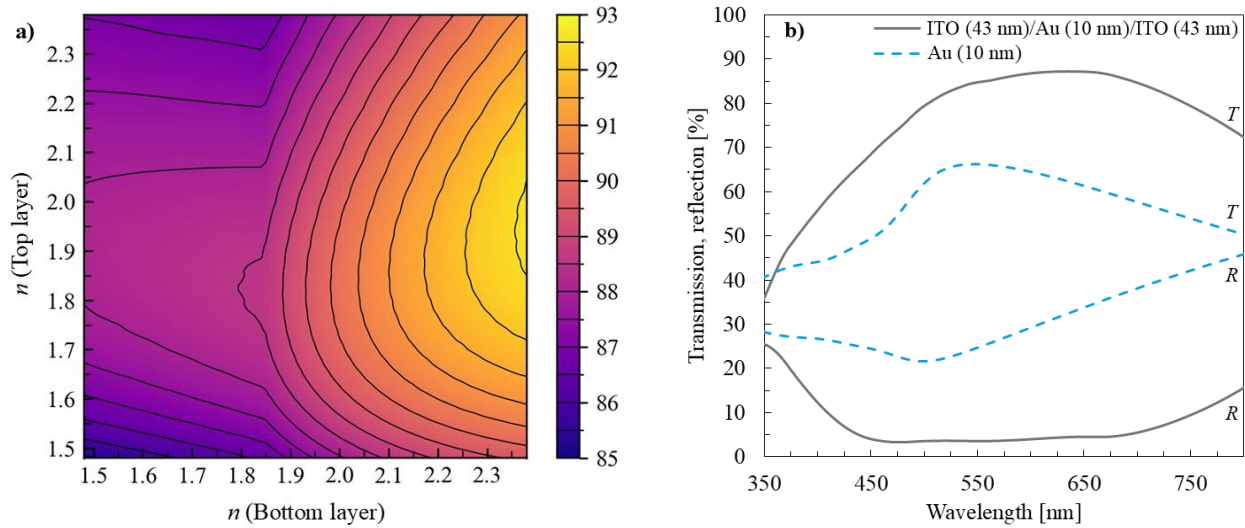


Figure 4.2: a) Map of the highest luminous transmittance obtained when varying the refractive indices of the top and bottom dielectrics in a tri-layer stack with a 10 nm Au middle layer, where the thicknesses of the dielectric layers are optimal. b) Comparison of the theoretical R and T obtained for a single gold layer and an optimized IMI stack, both deposited on PET substrates.

Following **Equation 4.2**, it is possible to calculate the impact the two ITO layers have on the overall sheet resistance of the electrode. Knowing that a 10 nm Au layer has a sheet resistance of $\sim 7 \Omega/\square$, again calculated from the measured resistivity of a 45 nm gold layer, the two ITO layers combined would lead to a mere $\sim 0.6 \Omega/\square$ decrease in the total sheet resistance. Although they do not contribute significantly to the overall conductivity, the bottom layer, as will be demonstrated further below, can provide improved gold growth conditions, and the top layer offers a conductive surface for the final electrode. Finally, ITO is chemically and mechanically robust, allowing for simpler manipulation and protection against scratching, both beneficial when considering the overall mechanical durability of the electrode.

$$\frac{1}{R_s} = \frac{1}{R_{s\text{ ITO}(1)}} + \frac{1}{R_{s\text{ Au}}} + \frac{1}{R_{s\text{ ITO}(2)}} \quad (4.2)$$

4.2.3.2 Single Gold Layer and IMI Electrodes

To maximize the transmission and conductivity of the electrode, it is primordial to optimize the deposition conditions and thickness of the conductive metal layer. Since gold was selected as the metallic material of the electrode, understanding its growth dynamics was crucial to obtain the highest conductivity at the lowest possible thickness, minimizing absorption and thus, maximizing transmission. Indeed, gold is known to grow in a Volmer-Weber growth mode, first starting as discontinuous islands, which then grow, coalesce and ultimately form a continuous thin film [40]. A minimum amount of gold must, therefore, be deposited before obtaining a conductive sample. Gold thin films of different thicknesses were thus deposited using the previously indicated deposition conditions (see **Table 4.1**). Following these tests, it was possible to determine that a thickness below ~5 nm led to a non-conductive sample. Note that modifying any single parameter, such as the type of substrate, the deposition temperature, the deposition rate, etc., will impact the growth dynamics of the films and thus change this minimum thickness value [113] [114].

As such, modifying the surface on which the gold films were deposited had a large impact on its optoelectronic performance; in the present case, comparing the deposition directly onto PET vs. encapsulated between two 43-nm-thick ITO films (see **Figure 4.3**). Indeed, simply depositing the gold films onto ITO significantly improved the sheet resistance. For example, a 10 nm film shows a drop of 7.4 $\Omega/\square$, a value much higher than the calculated decrease, which is expected by the addition of the ITO layers alone. Indeed, by using **Equation 4.2** and the sheet resistance values for the gold layer and the two ITO layers, 14.5 $\Omega/\square$ and ~180 $\Omega/\square$ respectively, a ~2 $\Omega/\square$ decrease is expected. The same trend can be observed for even lower thicknesses, where films of 4 nm still present acceptable conductivity. Hence, it seems that the ITO film acts as a seed layer for the growth of the gold film, promoting an earlier percolation threshold and overall improved optoelectronic properties. **Figures 4.3a** and **4.3b** show how, in both cases, the gold films deposited onto ITO are much closer to the predicted values, which suppose a perfectly continuous gold layer, than for gold deposited onto PET. In the case of **Figure 4.3b**, it is possible to see that the experimental transmission spectrum of an ITO/Au (4 nm)/ITO stack is much closer to its

theoretical spectrum in comparison to the experimental spectrum of a single 4 nm Au layer. In addition, the latter shows clear signs of plasmonic absorption at around 600 nm. All the above demonstrates that, at low thicknesses, the gold layer is more continuous when deposited onto ITO.

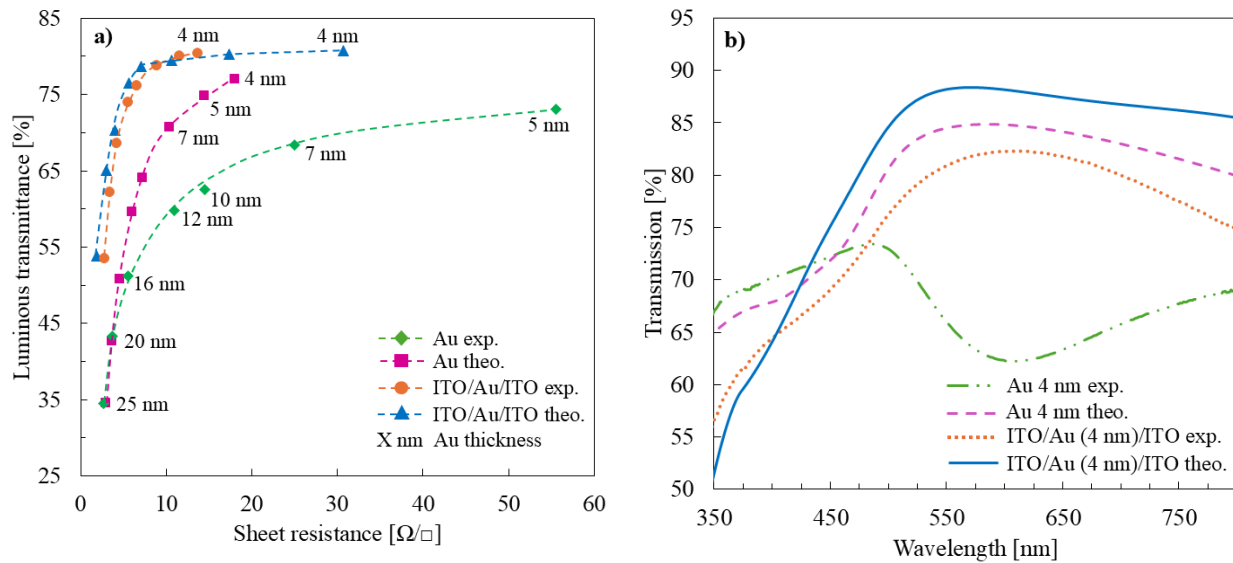


Figure 4.3: Theoretical and experimental a) optoelectronic properties for different gold thicknesses deposited directly onto PET or incorporated within an IMI stack, and b) transmission spectra for a single 4 nm Au layer and within an optimized IMI stack. The gold optical and electrical properties were those established for a 45-nm-thick film.

While in practice one would like to obtain an electrode with the highest possible transmission, a trade-off must be made. Indeed, when looking at the theoretical variation of transmission vs. sheet resistance (see **Figure 4.3a**), it is clear that these two properties are inversely proportional. On the other hand, significant gains in transmission can be obtained when working with a low thickness of Au while remaining in a range of acceptable sheet resistance values. However, the luminous transmittance never reaches above 80%.

This is the moment when the patterning of the electrode comes into play as a means of improving the overall transmission. However, a large portion of the gold will be removed when considering patterning. This will inevitably increase the sheet resistance, thus requiring thicker gold films. With the simulations presented in the following section, it will be possible to assess the increase in sheet resistance an electrode will possess when patterned. Combining the results with the above sheet

resistance as a function of thickness will allow one to estimate the necessary gold thickness to ensure an acceptable sheet resistance value.

4.2.3.3 Patterning of the Electrodes

Patterning represents an obvious solution to increase optical transmission. According to Sakamoto *et al.* [35], it can also help increase the flexibility of an electrode when submitted to bending tests. While patterning will inevitably increase the sheet resistance of the sample, choosing an appropriate size and type of pattern can help minimize this effect.

The luminous transmittance of the patterned electrode can be calculated via the following equation:

$$T_{\text{lum total}} = \text{NPA} \cdot T_{\text{lum PA}} + (1 - \text{NPA}) \cdot T_{\text{lum CA}}, \quad (4.3)$$

where NPA represents the normalized patterned area (PA) and CA the conductive area.

However, it is nontrivial to understand how patterning impacts the conductivity of a sample. To gain a better insight into the matter, simulations were run in *QuickField* (QF) to obtain the resulting current vs. voltage curves for different types of patterns for various NPAs. A fixed 8 cm by 8 cm simulation area, with top and bottom electrodes, was established within the software and defined as a conductive area with a chosen resistivity. Non-conductive regions (or PA) were added inside that area with different shapes to represent various patterns of interest: squares, circles, hexagons and lines (see **Figure 4.4**). Then, their size was increased, for each type of pattern, and the simulation was run with a 0.01 V potential difference. The resulting current could thus be obtained, the current for a complete CA (no patterns) serving as a baseline. Then, by combining these results with the known starting sheet resistance and luminous transmittance of a non-patterned sample, it is possible to judge how the type of pattern impacts these parameters. **Figure 4.4** shows the results for a 10 nm non-patterned gold film as a starting point. Each following point represents an increase in the size of the pattern, thus increasing the NPA. For example, the first points for each curve have no patterning, which represents a 0% ratio. Then, the following points show the ratio according to the size of the pattern starting at 0.125 and increasing by this value until 0.875. It is possible to observe that the line pattern results in the largest gain in transmission among the tested patterns.

For each type of pattern, there is always a range of normalized patterned areas that allows for a high increase in the luminous transmittance without significantly increasing the sheet resistance.

For all the tested patterns, this NPA is at ~ 0.75 . With this information in hand, it is possible to create masks with dimensions proportional to the ones above to achieve an optimal PA for each type of pattern. Note that the curves below are calculated for a given thickness of gold and that higher PAs could also be of interest if the starting sheet resistance was lower, e.g., by simply increasing the gold thickness or adding an ITO underlayer, as previously shown. While the above simulations led to the design of different masks consisting of circles, hexagons and squares, only square patterns with NPA values of 75% and 84.5% will be presented here, as no significant gains could be observed in terms of transmission vs. sheet resistance between these various patterns (see **Figure 4.4**). In addition, implementing a line pattern would lead to obvious issues in terms of flexibility. As such, and assuming that lined patterns offer the option of reaching higher luminous transmittance, a random line design with an NPA of 85% was also designed. **Figure 4.5** shows the key-designed masks with their respective dimensions.

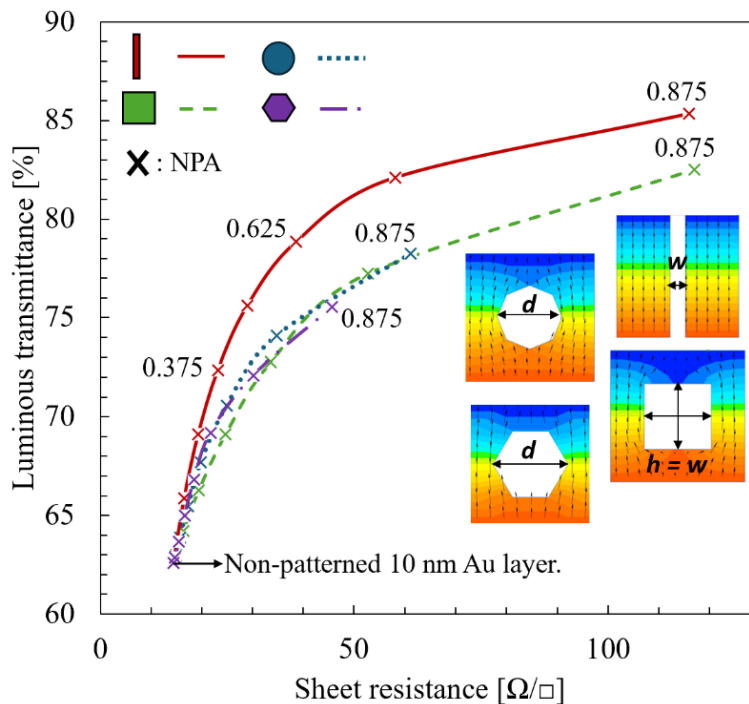


Figure 4.4: T_{lum} vs. R_s for different types and sizes of patterns following simulations in *QuickField*.

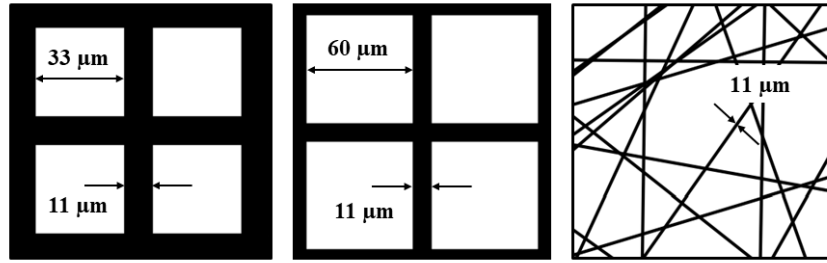


Figure 4.5: Various tested mask designs with their corresponding dimensions.

4.2.3.4 Combining the Above Approaches

The previous sections detailed the optimization process of IMI stacks, the deposition of the gold films as well as the impact of the size of the chosen pattern. Combining all of these approaches allows one to further enhance the performance of the electrode.

As expected from the different simulations and optimizations done in the previous sections, a significant increase in transmission can be achieved by combining an IMI stack and patterning. **Figure 4.6** presents the transmission and reflection curves for three different samples: a non-patterned gold layer, a non-patterned IMI stack, and a patterned IMI stack with the random line design, all with the same gold thickness of 20 nm and ITO thicknesses of 44 nm and 38 nm for the top and bottom layers, respectively.

When looking at the spectra, it can be observed that each step, IMI stack and then patterning, increases the transmission of the electrodes. Indeed, a gain of 23.4% can be observed at 550 nm when ITO layers of optimal thickness are added on top and under the Au film. This is followed by another increase of 16.5% at 550 nm when the tri-layer stack is patterned with random lines. However, this value is dependent on the pattern used and is thus subject to variations even for the same gold thickness. The reflection adheres to the same trend with a 30.7% decrease at 550 nm after the ITO layers addition. On the other hand, one can notice that, even though the transmission increases when patterning the IMI stack, the reflection does not decrease. This is due to the reflection of the exposed areas of the PET substrate, made bare in the patterning process. Therefore, by combining stacking and patterning, a total increase of 39.9% in transmission at 550 nm can be

obtained in comparison to a single 20 nm gold layer, where more than half (58.6%) of that increase is also produced without affecting the sheet resistance.

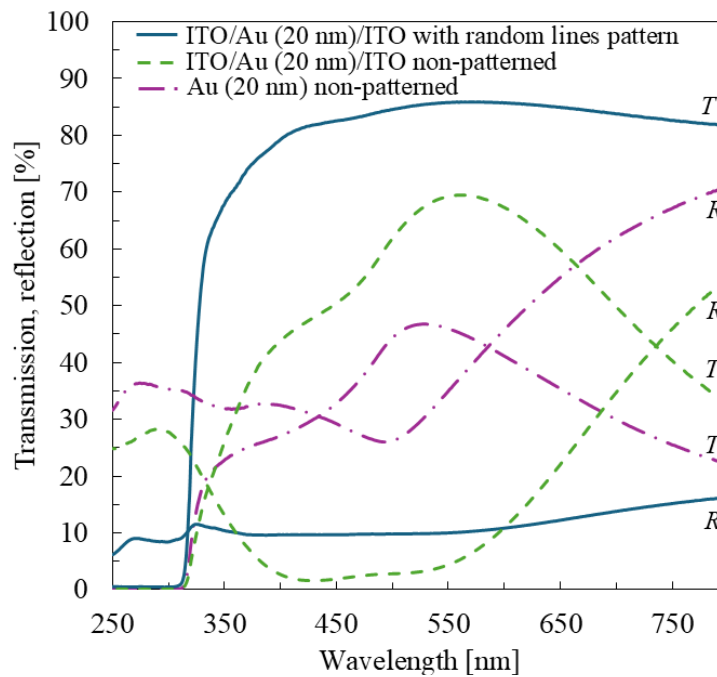


Figure 4.6: R and T spectra for a non-patterned gold layer, a non-patterned IMI stack and a patterned IMI stack with the random line design, all deposited on PET substrates and with a 20 nm gold thickness.

Table 4.2 summarizes the optoelectronic properties of the two different types and sizes of patterns as well as the ones of the blank PET substrate for reference. The scattering in transmission is also shown, as it can be considered important in some applications and is, unfortunately, rarely reported. For each sample, the Au thickness was optimized inside the IMI stack depending on the type of pattern implemented. Indeed, since the patterns have different ratios of patterned areas, the gold thickness needed to be adjusted so that all samples remained within the R_s target value of $50 \Omega/\square$ once patterned. It can be observed that, when implementing the optimal thickness, the different patterns lead to similar results in terms of sheet resistance and transmission, with the larger patterns, such as the random lines and the $60 \mu\text{m}$ squares, giving the best results ($R_s \leq 50 \Omega/\square$, $T \geq 90\%$). Note that the transmission reached above 90% by combining the random line design and a PET substrate that had been previously coated with an anti-reflective layer of MgF_2 on the backside. This sample, as well as the $60 \mu\text{m}$ square pattern, blank PET substrate and non-patterned IMI stacks, are presented in **Figure 4.7**.

Table 4.2: Optoelectronic properties for different types of patterns with optimized gold thicknesses in an IMI stack.

Pattern type	T at 550 nm [%]	S_T at 550 nm [%]	R_s [$\Omega/\square$]	Simulated T and R_s [% $\Omega/\square$]		Au thickness [nm]
Blank PET	88.6	1.2	-	-	-	-
Blank PET with MgF_2 coated backside	93.7	1.2	-	-	-	-
Squares 33 μm	84.3	2.4	45.0	83.7	40	10
Squares 60 μm	85.2	0.8	39.4	85.4	42	11
Random lines	85.8	1.7	49.0	85.6	24	20
Random lines with MgF_2 coated PET on backside	90.3	1.8	49.0	90.1	24	20

With a scattering in transmission at 550 nm at 0.8%, the large squares offer the best results regarding their optoelectronic properties. However, further testing with the different patterns revealed that the squares produced diffraction patterns, which can be expected when working with highly ordered structures (see **Figure 4.7d**). This is what prompted the random line pattern design, which, indeed, did not show any signs of diffraction (see **Figure 4.7h**). Lowering the line width of the patterns could potentially be beneficial in this respect; however, in the present case, we were limited to 10 μm by the chosen photomask printing process.

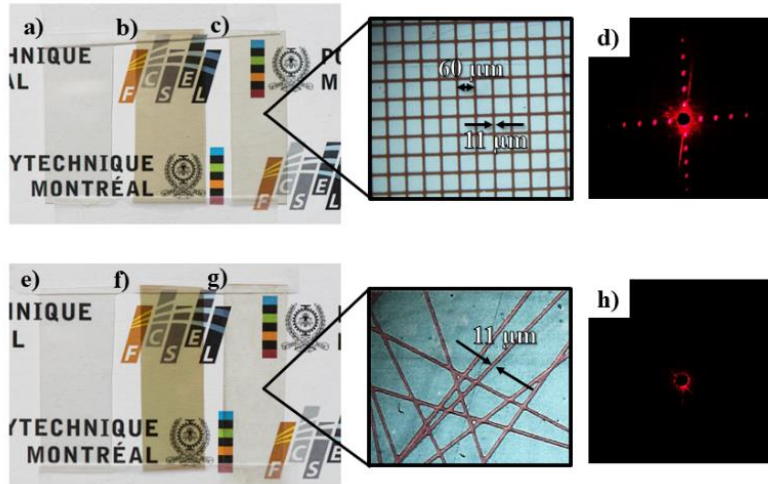


Figure 4.7: 60 μm squares (top) and random lines (bottom) where a) and e) correspond to a photo of a blank PET substrate, b) and f) are the non-patterned IMI stacks, c) and g) are the patterned sample with an MgF_2 coated backside for g), and d) and h) are the corresponding diffraction patterns for their respective patterns.

Table 4.2 also presents the simulated transmission and sheet resistance values obtained by combining the *QuickField* simulations with the measured sheet resistance and transmission from non-patterned IMI stack samples with the corresponding gold thicknesses. It is important to note that in the case of the random lines, the pattern simulated on *QF* was a single line, making a comparison between the fabricated sample and the expected values much less accurate. For the square patterns, it is possible to observe that the expected transmission is situated at a maximum difference of 0.6% from the measured transmission of the patterned samples. The sheet resistance values are also quite close in the case of the square patterns, with a maximum deviation of 5 $\Omega/\square$. As expected, the simulated sheet resistance values for the random lines are further from the measured ones.

Figure 4.8 compares the optoelectronic performance of the fabricated random line electrodes to the ones of gold-based electrodes found in the literature. It can be observed that the presently proposed electrodes offer higher performance than most of what has been proposed until now. Indeed, it can be observed that gold electrodes having above 90% transmission possess sheet resistance values above 100 $\Omega/\square$, whereas electrodes with a sheet resistance below 50 $\Omega/\square$ offer a maximum transmission of around 80%. The proposed random line electrodes, while being in the previously mentioned range of sheet resistance, manage to reach almost 86% in transmission at

550 nm when deposited on PET substrates. It is also important to note that the comparison electrodes shown in **Figure 4.8** were not all deposited on PET substrates, and as such, the final transmission values may not be directly comparable.

It was thus also interesting to evaluate the performance of the electrodes when fabricated on a backside-AR-coated PET substrate, which increased its transmission above 90%. Doing so allowed us to reach the target ranges for both T and R_s . Furthermore, the random line pattern proposes a similar structure as nanowires, a popular method to create FTEs with gold, silver and other materials, but avoids issues such as non-uniformity and surface roughness as well as being more suited for large-scale applications, particularly since the methodology can be adapted to roll-to-roll coating [115].

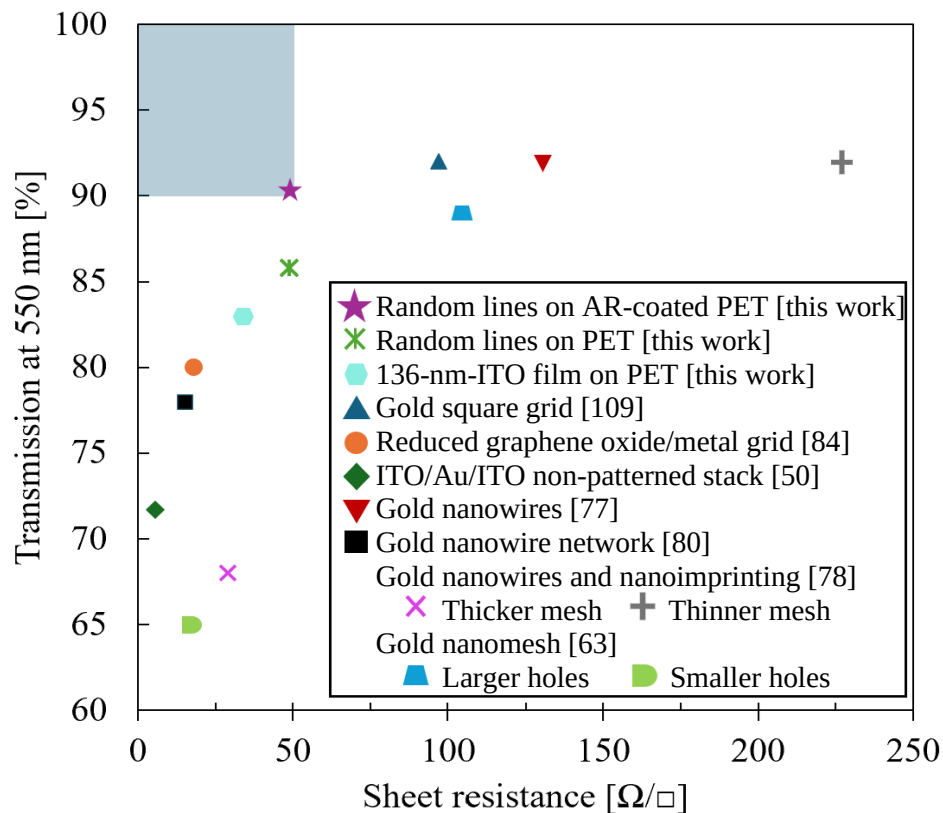


Figure 4.8: Optoelectronic performance of the highest performing transparent and flexible electrodes obtained in the present work compared to gold-based electrodes found in the literature.

Testing for Flexibility

To assess the flexibility of the samples, two types of tests were performed. In the first test, the sheet resistance variations were observed for different diameters of curvature (d) to determine the minimum value that a sample could reach before it displayed conductivity changes. For the second test, the minimum diameter of curvature was fixed to a set value, and the sample was submitted to 1000 bending cycles, when d was varied from the minimum value to d plus 20 mm. In both tests, the samples were placed so that the coatings would be submitted to tensile stresses.

To evaluate the impact the patterns and choices of materials had on the flexibility of the electrodes, three iterations of the tests were made. To begin, a non-patterned sample of 120 nm of ITO was compared to two patterned square samples (33 μm and 60 μm), also made from 120 nm of ITO, to see if, as Sakamoto *et al.* showed, patterning helped with the overall flexibility of the samples [35]. Afterward, the same non-patterned ITO sample was compared to one fabricated with a non-patterned ITO/Au/ITO stack, in order to assess the differences an encapsulated gold layer has on the flexibility of the electrode. Finally, the flexibility of patterned electrodes fabricated from IMI stacks was also investigated to obtain the performance of the final prototypes.

Figure 4.9 presents the flexibility results for the patterned ITO samples. It is first possible to observe that the patterning indeed helped with the overall flexibility of the samples (see **Figure 4.9a**), by allowing the patterned electrodes to reach a lower diameter of curvature before experiencing any changes in resistance, as demonstrated in **Table 4.3**. The better performance of the 33 μm square sample can be explained simply by its higher density of conductive lines, which is ~61% higher than in the 60 μm square design.

While the non-patterned ITO sample remained conductive throughout the whole bending process, surprisingly, the two patterned ones did not once they reached a d of 8 mm. Literature reports that patterning can help lower the tensile stress in the electrode while also stopping crack propagation [35]. However, during patterning, a large portion of the coating is removed (between 75% and 85% in the present case), decreasing the amount of available conductive area. Since patterning does not stop crack formation, once the electrode reaches a specific diameter of curvature, where cracks have developed over the majority of its conductive area, it becomes non-conductive. On the other hand, its non-patterned counterpart still remains conductive, though with much higher sheet resistance than its initial value. We surmise that this phenomenon is less depicted in the literature,

as it requires one to reach very small diameters of curvature ($d \leq 8$ mm), which is often not achievable, either because of substrate/electrode and/or instrument limitations.

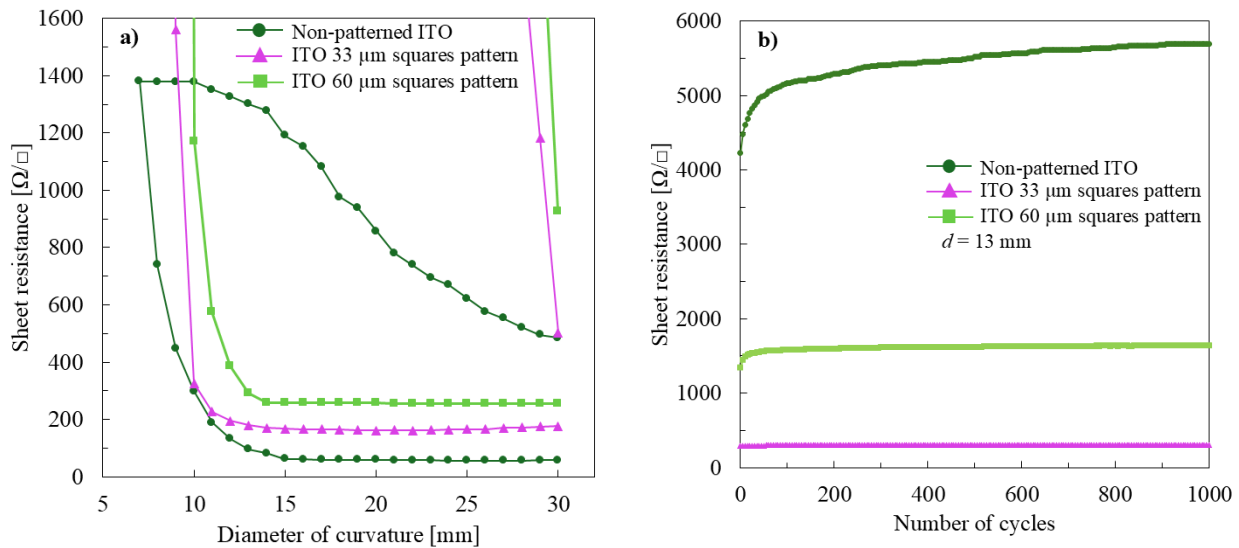


Figure 4.9: Flexibility tests for patterned and non-patterned 120-nm-ITO samples where a) the diameter is varied from 30 mm down to 7 mm and vice versa and b) the minimum diameter is fixed at $d = 13$ mm, and 1000 bending cycles are performed (between d and $d + 20$ mm).

Table 4.3: Key flexibility results for 120-nm-ITO-based electrodes with and without patterns.

Sample	$d_{\min}$ with no cycles [mm]	R_s at $d = 7$ mm with no cycles [$\Omega/\square$]	R_s at $d = 13$ mm with no prior cycles [$\Omega/\square$]	R_s before and after 1000 cycles at $d = 13$ mm [$\Omega/\square$]	
Non-patterned	15	1380	96	4232	5691
33 μm squares	13	Non-conductive	170	300	300
60 μm squares	14	Non-conductive	293	1340	1644

Finally, **Figure 4.9a** shows a sheet resistance decrease for every sample when the diameter of curvature starts increasing. In the case of solely ITO-based electrodes, this R_s decrease brings the patterned electrodes back into a conductive range, or simply closer to their original conductivity. In the case of tri-layer electrodes, patterned or not, the sheet resistance is even brought back to its

original value upon reaching a certain diameter of curvature, as it will be demonstrated shortly. After looking at samples bent at different d values under an optical microscope (see Supporting Information document), it was found that this phenomenon occurred due to the creation of small cracks at low diameters of curvature, which then fit back together, to a certain extent, depending on the sample, during the subsequent increase in radius of curvature.

Figure 4.9b illustrates the sheet resistance changes that the different ITO-based electrodes undergo when submitted to 1000 bending cycles at $d = 13$ mm. When comparing the three samples, it is clear that the patterns help in maintaining a more stable resistance during cycling. Indeed, the 33 μm square electrode can endure 1000 bending cycles with no resistance changes, compared to the non-patterned ITO, which sustained an increase of over 1000 $\Omega/\square$ in sheet resistance, as detailed in **Table 4.3**. The 60 μm sample also performs better than the latter, with a ~ 300 $\Omega/\square$ increase registered over the 1000 cycles. The difference between the two patterned samples can again be explained by the variation in the line density, where the same trends were observed in the ITO electrodes fabricated by Sakamoto *et al.* [35]. For all three samples, cycles were made at $d = 15$ mm, $d = 14$ mm and then at $d = 13$ mm, the results of which are shown in **Figure 4.9b**. This sequence demonstrates that cycling seems to accelerate the crack formation and/or propagation. Indeed, it is possible to see from **Table 4.3** that, for all three samples, the sheet resistance is higher than what was obtained for the same diameter with no prior cycling, with the non-patterned ITO sustaining the larger increase by far. This further demonstrates how patterning can have a positive impact on the flexibility of the electrodes.

To continue, the flexibility of the non-patterned 120-nm-ITO electrode was compared to the one of a non-patterned electrode made with an IMI stack (ITO (40 nm)/Au (11 nm)/ITO (43 nm)), the results of which are depicted in **Figure S4** available in the Supporting Information document along with the key results for the flexibility tests of the non-patterned IMI stack (see **Figure 5.3** and **Table 5.1** for the thesis). As a summary, it is observed that the tri-layer stack undoubtedly produces added benefits to the flexibility of the electrode, as d_{min} and the maximum sheet resistance increase (with and without cycles) were all much lower than the ones of the reference non-patterned ITO-based electrode.

The last iteration of the tests was performed to assess the flexibility of the different patterned tri-layer electrodes. As such, four samples were compared: a 60 μm square pattern, a 33 μm square

pattern and two random line (RL) patterns (see **Figure 4.10**). The squares and the first random lines all had identical architectures, i.e., ITO (40 nm)/Au (11 nm)/ITO (43 nm), the same thicknesses that were used in the non-patterned sample presented in the Supporting Information document, as a means of comparing the samples solely on their differences of pattern and not on material variations. The second random line pattern had an optically optimized IMI stack of ITO (38 nm)/Au (20 nm)/ITO (44 nm), prepared with a thicker gold layer so that the sheet resistance was below $50 \Omega/\square$.

Figure 4.10a demonstrates how much of an impact the choice of pattern can have on the overall flexibility of the sample. Indeed, when looking at the $60 \mu\text{m}$ and $33 \mu\text{m}$ square patterns, the samples are non-conductive at $d = 7 \text{ mm}$, while both random line patterned samples are still conductive, with R_s even below $90 \Omega/\square$ for the 20 nm Au sample, as it can be seen in **Table 4.4**. It is important to highlight that the sheet resistance of the 11 nm stack was much higher to start with, thus explaining the more important sheet resistance changes, even though the relative increase is similar for both random line samples. These same samples also reached a lower $d_{\min}$ compared to both square designs (see **Table 4.4**), thus making the random line patterned electrodes more flexible overall.

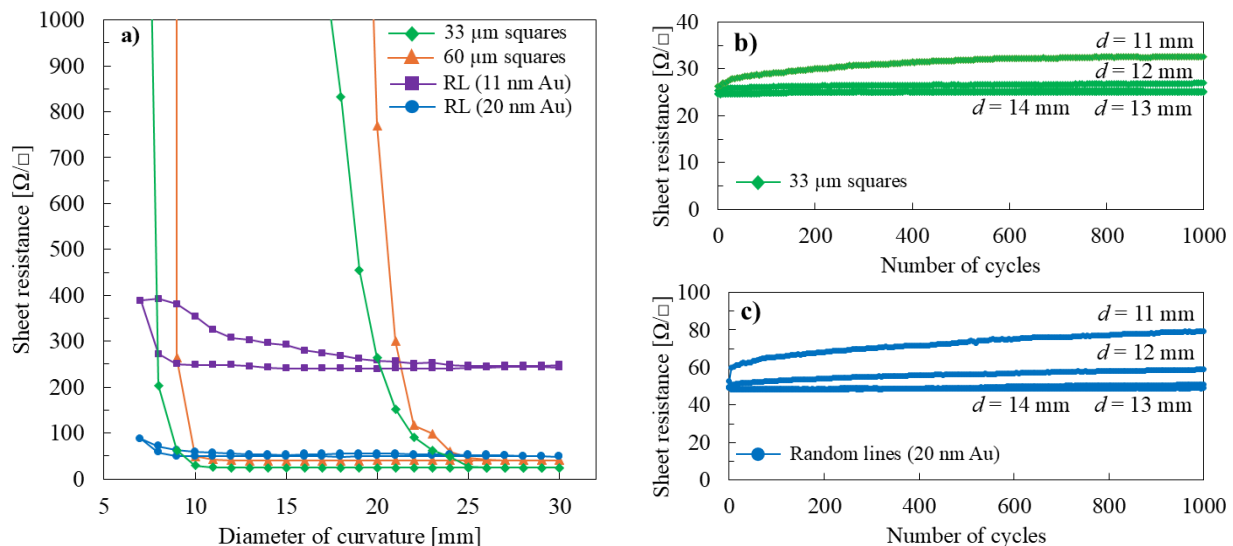


Figure 4.10: Flexibility tests for different patterned tri-layer electrodes where a) the diameter is varied from 30 mm down to 7 mm and vice versa, and b) and c) the minimum diameter is fixed at a given d value, and 1000 bending cycles are made for each one (between d and $d + 20 \text{ mm}$). Note that the acronym RL is used to designate the random line pattern.

Table 4.4: Key results for the flexibility tests of the various IMI patterned electrodes.

Sample	Initial R_s with no cycles or bending [$\Omega/\square$]	$d_{\min}$ with no cycles [mm]	R_s at $d = 7$ mm with no cycles [$\Omega/\square$]	$d_{\min}$ with 1000 cycles [mm]	R_s at $d_{\min} - 1$ mm with 1000 cycles [mm $\Omega/\square$]	
33 μm squares	24	11	Non-conductive	13	12	27
60 μm squares	40	11	Non-conductive	-	-	-
Random lines (11 nm Au)	247	9	388	-	-	-
Random lines (20 nm Au)	49	9	87	13	12	59

Taking a look back at **Table 4.3**, it is interesting to note that for the same square patterns, a lower $d_{\min}$ was achieved when the electrode was made from the tri-layer stack rather than the single ITO layer, proving once again the positive impact an encapsulated gold layer can have on the flexibility of the electrodes. Additionally, as observed previously, the different patterned samples start converging towards their original sheet resistance values once d starts increasing, with all samples reaching it beyond $d = 27$ mm.

Figures 4.10b and **4.10c** show how the flexibility of the different patterned electrodes is affected by performing multiple bending cycles. For these figures, only the 33 μm square sample and the random line patterned sample with 20 nm of Au were chosen for the 1000 cycles bending tests, as the same types of patterns displayed similar results. As observed in the previous samples, resistance changes start to appear at a greater d compared to the flexibility tests without cycling, giving a higher $d_{\min}$ as shown in **Table 4.4**.

From the flexibility results highlighted in this section, it is clear that combining patterning and an IMI stack helps increase the overall flexibility of the electrodes to a level the individual techniques could not reach, further justifying the interest in the presented fabrication methodology.

4.2.4 Conclusions

A durable patterned tri-layer flexible and transparent electrode has been developed using a combination of stacking and patterning. Gold was used as the conductive layer and was placed between two ITO layers in the form of an IMI stack. The stack allowed for a 14.75% theoretical increase in luminous transmittance in the case of a 10 nm Au layer, and the presence of the ITO layers provided better gold growth as well as a conductive top layer for the electrode. The IMI stack was then patterned to further improve the transmission of the electrode in addition to its flexibility. The random line pattern proved to be the one offering the best compromise in terms of conductivity, transmission and flexibility. This pattern led to a transmission of 90.3% at 550 nm with a sheet resistance of $49 \Omega/\square$ on a backside anti-reflective-coated PET substrate or 85.8% on a regular PET substrate.

The random line sample also exhibited relatively low scattering (below 2%) and did not show, as expected, any signs of diffraction. Regarding the flexibility, this pattern allowed the electrode to reach a diameter of curvature of 9 mm before showing any signs of an increase in the sheet resistance, which, at a maximum, only increased to $87 \Omega/\square$. The electrode was also able to support 1000 cycles for a minimum diameter of curvature of 14 mm without significant changes in its sheet resistance. For minimum diameters below 14 mm, it sustained a progressive increase in sheet resistance, gaining in amplitude as the diameter decreased. The combination of ITO and gold as the materials for the electrode allowed for better overall durability to manipulation and scratches than a single metal layer electrode.

With this new type of durable transparent and flexible electrode, different applications, such as wearable electronics or optoelectronics, will be able to undergo interesting improvements leading to new innovative technologies and more scientific progress. For further improvements, the masks could be reworked to allow for finer lines, potentially allowing for higher line densities without impacting the transmission of the electrode, the latter also helping with the overall flexibility of the electrode. Finally, by combining finer lines with a thicker gold layer, it could also be possible to improve the transmission of the electrode without affecting its sheet resistance.

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CHAPTER 5 GENERAL DISCUSSION

5.1 Forward

This chapter presents a general discussion composed of additional results, comments and comparisons that are complementary to the ones presented in the article. The first two sections cover the findings that were reported in the Supporting Information document mentioned above. The other three sections of this chapter present information that was not sent for publishing but was still relevant to the successful completion of the project. To start, more details are given on the use of MgF_2 as an anti-reflective coating for the PET substrates. Then, this chapter presents the results that were obtained for a tri-layer electrode made with a $\text{TiO}_2/\text{Au}/\text{ITO}$ stack, an alternative to the IMI one shown in the article. Finally, while the paper focused on three patterns, a total of eight were tested during the project. Therefore, the optoelectronic and flexibility performance from those additional patterns is also presented here and compared to the ones in the article.

5.2 Cracking

As demonstrated in Section 4.2.3.4 of the article, an interesting phenomenon occurs when the diameter of curvature re-increased following the bending of the electrodes. Indeed, by looking at the different graphs (**Figures 4.9a, 4.10a**, or even **5.3a** in Section 5.3), it is first possible to see that the sheet resistance increases when the sample is bent under different diameters of curvature. The latter changes depending on the samples, but an increase is inevitably obtained in all cases. However, when d starts going back to greater values, a lowering of the sheet resistance can be observed where, in some samples, it even decreases back to its original value. When presented with those results, it was decided to further investigate the cause by looking at a bent sample under an optical microscope as described in Section 3.5.1.4.

Figure 5.1 presents the images obtained for an ITO (40 nm)/Au (11 nm)/ITO (43 nm) stack combined with a 60 μm square pattern, where the sample was bent to different diameters of curvature. Note that the same square was focused on during the d variations, allowing for more accurate observations, but all squares showed similar results.

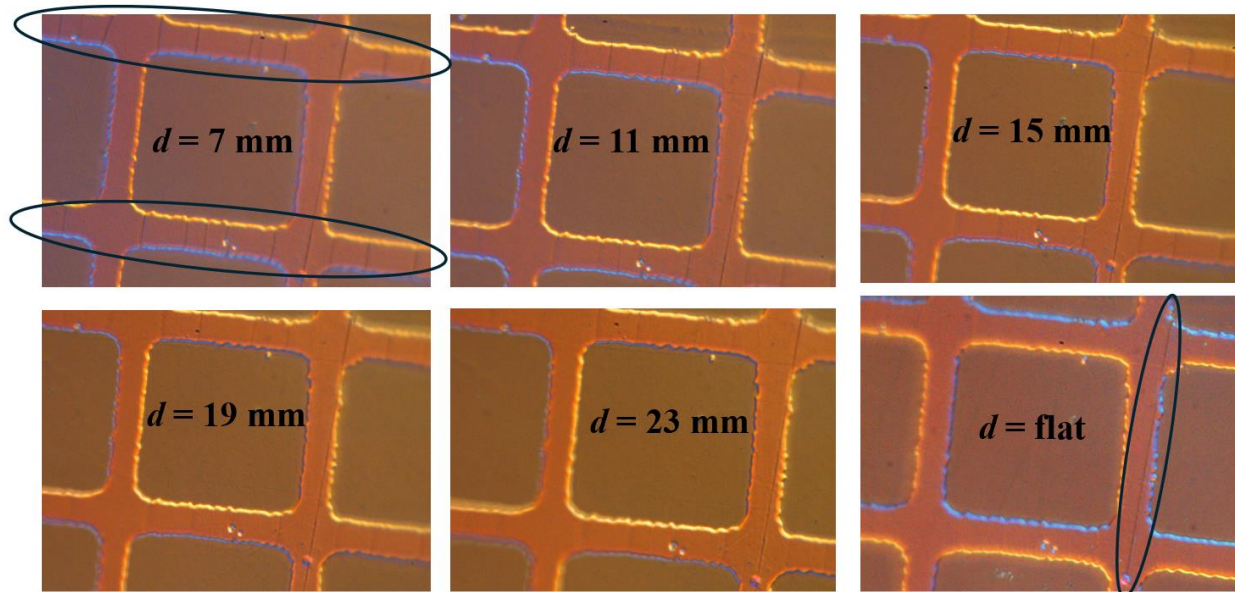


Figure 5.1: Optical microscope pictures of a 60 μm square patterned ITO (40 nm)/Au (11 nm)/ITO (43 nm) sample bent at different diameters of curvature. The same square was observed for all the pictures. Dark ellipses showcase cracks of interest.

From **Figure 5.1**, it is first possible to observe the presence of many small cracks, formed perpendicularly to the applied force, at low diameters of curvature (see horizontal ellipses in **Figure 5.1**). These cracks impact the conductivity of the sample, explaining the sheet resistance increase at low d values. However, when comparing the different images during the increase in the diameter of curvature, the small cracks start to disappear progressively, even becoming invisible when the electrode is once again lying flat. This phenomenon, combined with the resistance decrease observed in the graphs, leads us to believe that the small cracks essentially fit back together like in a puzzle. This allows current to circulate once again in these previously poorly conductive areas, decreasing the overall sheet resistance of the electrode.

The second observation that can be made from **Figure 5.1** is that larger cracks are not prone to the same amount of restoration as the smaller ones. Indeed, on the right side of the square (see dark vertical ellipse on the bottom right of **Figure 5.1**), a larger crack can be observed throughout the

different diameters of curvature, showing that even though the crack fades slightly, it is still quite visible even when the electrode is not bent. However, since the crack only obstructs one or two paths out of the multitude of available ones, the overall sheet resistance of the sample can remain low. Furthermore, it is interesting to note that multiple bending cycles might reduce the ability of the cracks to fit back together, resulting in a sample with higher resistance even when returned flat.

As mentioned previously, SEM could not accommodate bent electrodes; however, some pictures of the flat sample were taken to have an even clearer look at the coating after bending. **Figure 5.2** presents those images, where the left image was taken on a tabletop SEM available at the Centre de recherche sur les systèmes polymères et composites à haute performance (CREPEC) at Polytechnique Montréal and the right one was taken on a Quattro SEM, available at the Centre de caractérisation microscopique des matériaux (CM)², also at Polytechnique Montréal. Even though the overall sample was conductive, the patterning created large non-conductive areas, which led to charge accumulation and lower-quality images. As a result, the right image was taken in environmental mode, which implies a lower vacuum and, thus, higher pressure. Note that while the same sample is shown here and above, the same square was not used in the SEM pictures.

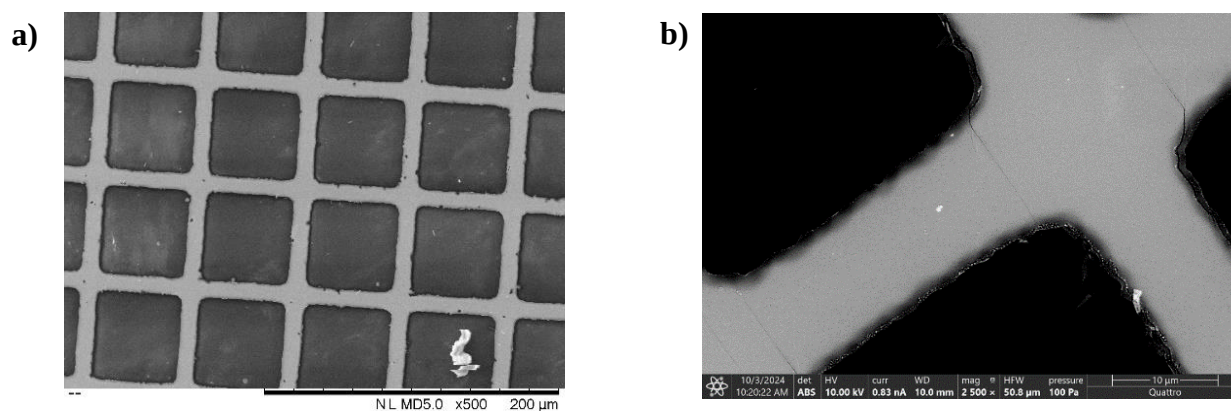


Figure 5.2: SEM pictures of the flat 60 µm ITO (40 nm)/Au (11 nm)/ITO (43 nm) electrode shown in **Figure 5.1** where a) was taken on a tabletop SEM and b) on a Quattro SEM in environmental mode.

The first image, taken at a lower magnification, shows no evident signs of cracking in the coating. However, as shown in b), some faint cracks can be observed when the magnification increases. When comparing the latter with the images in **Figure 5.1**, there is no doubt that some of the cracks observed above for a bent sample are still not visible with SEM imaging, further supporting the

aforementioned hypothesis of coating restoration (crack refitting). However, some larger cracks are still visible near the corners of the squares, which seems to generate more severe cracking than the edges, as the more significant damage was also observed alongside the corners in **Figure 5.1**.

5.3 Flexibility of a Non-Patterned IMI Stack

As mentioned in the article, two flexibility tests were performed for various types of electrodes. Among these samples, a non-patterned ITO (40 nm)/Au (11 nm)/ITO (43 nm) stack was compared to a non-patterned 120-nm-ITO-based electrode to assess the differences an encapsulated gold layer had on the sample's flexibility. The results of these flexibility tests are presented in **Figure 5.3**, and the key outcomes are highlighted in **Table 5.1**.

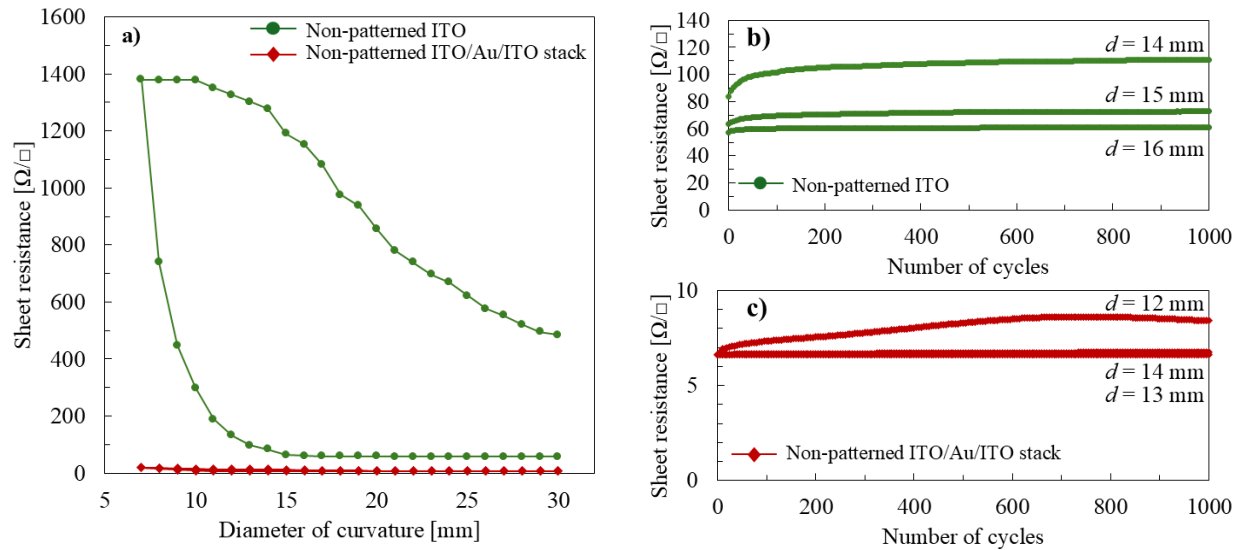


Figure 5.3: Flexibility tests for two non-patterned samples: a 120-nm-ITO electrode and an ITO (40 nm)/Au (11 nm)/ITO (43 nm) electrode, where, a) the diameter is varied from 30 mm down to 7 mm and vice versa and, b) and c) the minimum diameter was fixed at a given d value, and 1000 bending cycles are made for each one (between d and $d + 20$ mm).

It can be observed from **Figures 5.3a**, **5.3b** and **5.3c** that the tri-layer stack undoubtedly produces added benefits to the flexibility of the electrode. As indicated in **Table 5.1**, the presence of the flexible gold layer helps keep a low R_s even at $d = 7$ mm. The same sample reached a $d_{\min}$ of 11 mm, 4 mm lower than the one obtained with the non-patterned ITO. In **Figure 5.3a**, one can also notice

that the sheet resistance of the tri-layer sample goes back to its original value when d is increased, as previously mentioned in the article and explained in detail in Section 5.2.

Table 5.1: Key flexibility results for a non-patterned 120-nm-ITO-based electrode and a non-patterned ITO (40 nm)/Au (11 nm)/ITO (43 nm) stack electrode.

Sample	$d_{\min}$ with no cycles [mm]	R_s at $d = 7$ mm with no cycles [$\Omega/\square$]	$d_{\min}$ with 1000 cycles [mm]	R_s before and after 1000 cycles at $d = 14$ mm [$\Omega/\square$]	
ITO	15	1380	16	83	111
IMI stack	11	19	13	6.6	6.6

Figures 5.3b and **5.3c** present how cycling affects both types of samples for different diameters of curvature. Similar to the samples shown in the article, the IMI stack electrode is also subject to earlier damage when submitted to cycling, with $d_{\min}$ increasing to 13 mm. That being said, the IMI stack still demonstrates much better performance during cycling than the single ITO layer, with low to no sheet resistance increase for the same diameters of curvature.

5.4 Anti-Reflective Coating

During the project, the electrodes were primarily deposited on PET substrates, since they are well suited for flexibility testing. PET is also transparent, with a measured luminous transmittance of 88.6%. However, with the objective of reaching 90% or above T_{lum} for the fabricated electrodes, the transmission of the PET proved to be a limiting factor due to most of the PET being exposed by the patterning.

To improve the transparency of substrates, anti-reflective coatings can be used to lower the reflection and thus increase the overall transmission. MgF_2 is often used as an anti-reflective coating and can also be easily deposited via e-beam evaporation, which is why it was selected for the project. As presented in **Figure 5.4a**, coating only one side of the PET substrate with MgF_2

helped increase its overall transmission, bringing the luminous transmittance to 93.6% and thus above 90%.

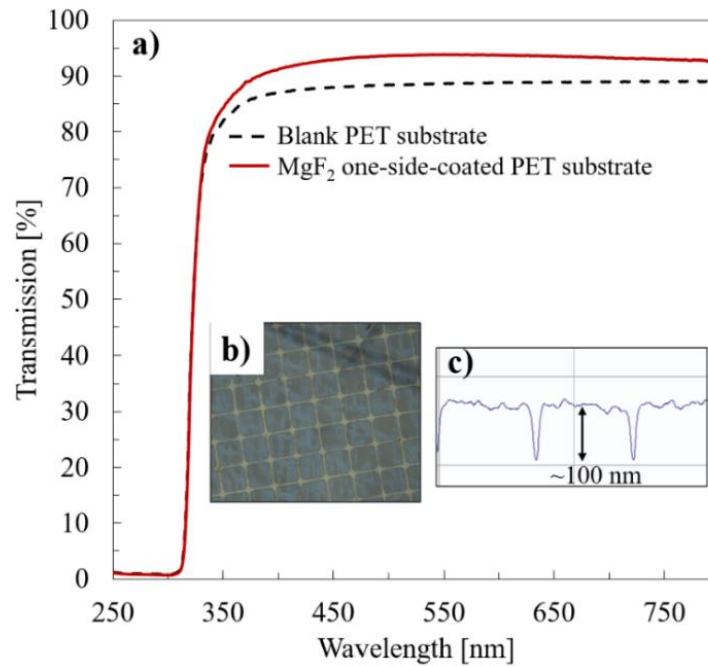


Figure 5.4: a) Transmission spectra of a blank PET substrate and a MgF₂ one-side-coated PET substrate. b) Optical microscope image of an IMI 60 μm square patterned electrode fabricated on top of a MgF₂ frontside-coated PET substrate. c) Profilometric measurements of the sample image in b).

The initial idea was to have a non-patterned MgF₂ layer deposited on the PET substrate, onto which the patterning and stacking methodology would take place, as explained in Chapter 3. However, adherence issues between the PET and the MgF₂ layer arose during the lift-off process. Indeed, all the lines in the pattern, i.e., the sections where the ITO/Au/ITO stack was usually deposited on the substrate, or in this case, on the MgF₂, were partially or completely gone after the lift-off. This left the sample with a square pattern but with bare PET lines and MgF₂-coated squares (see **Figure 5.4b**), thus totally non-conductive. This was also confirmed by profilometric measurements, where it was observed that the lines were at a lower height than the squares by ~ 100 nm, the deposited thickness of MgF₂ (see **Figure 5.4c**). These results led us to believe that the deposition of the IMI stack was causing a build-up of stress in the MgF₂, which lowered its adherence to the PET substrate to the point where it delaminated during the lift-off. However, with the project coming to an end, no further investigation was made, and it was decided to simply coat

the backside of the PET, which still gave a one-side-coated improvement in the transmission while bypassing the adherence issues. This was performed on the best sample, the tri-layer stack with the random line pattern, the results of which are presented in the article.

5.5 TiO₂/Au/ITO Stack

Figure 4.2a of the article presents a mapping of the highest luminous transmittance obtained when varying the refractive indices of the top and bottom dielectrics in a tri-layer stack with a 10 nm Au middle layer and where the thicknesses of the dielectric layers are optimal. It can be observed that the best transmission values are obtained when the bottom layer has a high refractive index above 2.2 and the top layer between 1.9 and 2.0 (1.98 being the optimal value). The ITO deposited via magnetron sputtering had a refractive index of 1.94 at 550 nm and was thus promptly chosen as the material for the top layer. For the bottom layer, TiO₂ deposited via electron beam evaporation was a good candidate with its 2.39 refractive index at 550 nm. Even though TiO₂ produced, theoretically, the stack with the highest luminous transmittance, ITO was selected for the bottom layer to simplify the development process, since it would have required two deposition techniques and a vacuum break. The deposition of TiO₂ could also have been done by MS, but it would have required optimizing the deposition parameters, which takes time. However, in the interest of thoroughness, some preliminary experiments were still conducted with a TiO₂/Au/ITO stack, where the TiO₂ was deposited via e-beam evaporation, to compare its performance to the ITO/Au/ITO one.

Figure 5.5 compares the R and T spectra of the previously mentioned stacks. The TiO₂ was deposited with electron beam evaporation, while the gold and ITO were done via magnetron sputtering. In both stacks, the thickness of the gold layer was fixed at 10 nm, and the surrounding layers were optimized with *OpenFilters*. Both samples were non-patterned and on PET substrates. While the simulations predicted a better luminous transmittance for the stack containing TiO₂, it is possible to see in **Figure 5.5** that the experimental data differs slightly. The transmission is indeed higher around 600 nm, but a steep drop is observed for the wavelengths below 500 nm, contributing to an overall lower luminous transmittance of 77.7% compared to 78.5% for the stack with two ITO layers. The difference between the experimental and theoretical values can most likely be explained by the deposition of the TiO₂, which is quite sensitive to the speed at which the current

was applied due to outgassing. Since the depositions were done manually, the speed was always approximative, and even though the pressure was monitored, it could have created variations in the concentration of O_2 , affecting the film's structural and morphological properties. However, the way gold grows on TiO_2 compared to ITO could have also affected the transmission of this layer and thus changed the transparency of the stack.

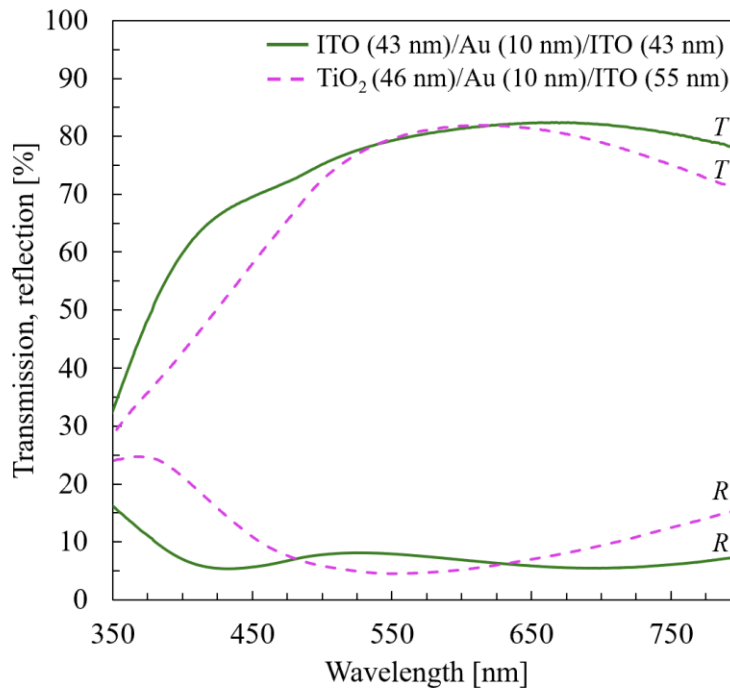


Figure 5.5: Comparison of the experimental R and T obtained for two 10-nm-gold-optimized-stacks on PET substrates: ITO/Au/ITO and TiO_2 /Au/ITO.

On the same subject, the article also detailed how ITO served as a good seed layer, promoting better gold growth, and thus, improved optoelectronic properties. **Table 5.2** compares the sheet resistance values obtained with the two non-patterned stacks presented above. A difference of $5.8 \Omega/\square$ can be observed, showcasing that the TiO_2 does not have the same properties as ITO for promoting an earlier percolation threshold during the growth of the gold layer. Two $33 \mu m$ square patterned electrodes were also fabricated, with one for each stack, and their respective sheet resistance is also shown in **Table 5.2**. While the sheet resistance of the patterned electrode with two ITO layers is below $50 \Omega/\square$, it is not the case for the one with TiO_2 . Thus, to obtain an electrode that respects the sheet resistance target, it would be necessary to increase the gold thickness, which would, in turn, be detrimental to the luminous transmittance. Therefore, combining all those results

demonstrates that ITO was the right choice for the bottom layer not only due to the simplification of the methodology but also because it led to better optoelectronic performance in the fabricated electrodes.

Table 5.2: Sheet resistance of non-patterned and 33 μm square patterned electrodes made with an ITO/Au (10 nm)/ITO stack and a TiO_2 /Au (10 nm)/ITO stack, both with optimized thicknesses.

Type of stack	Non-patterned	33 μm square patterns
ITO/Au (10 nm)/ITO	7.1 $\Omega/\square$	45.0 $\Omega/\square$
TiO_2 /Au (10 nm)/ITO	12.9 $\Omega/\square$	77.1 $\Omega/\square$

5.6 Additional Patterns

The article presented above highlighted the results for three types of patterns. While those patterns led to the best optoelectronic performances, it is still interesting to look at the other patterns tested during the project. Those can be divided into three categories: shifted squares, circles, and hexagons, both placed in a hexagonal array and random squares.

The shifted square masks consisted of the same sized squares (33 μm and 60 μm) and lines (11 μm) as the designs presented above, but rather than having the squares linearly on top of one another, they were shifted, resembling more a brick wall (see **Figure 5.6** for the example of the 33 μm squares). This new design aimed to further limit crack propagation, thus improving the overall flexibility of the electrodes. Additionally, since the squares and lines were of the same size, the optoelectronic properties were expected to remain similar to the regular square designs.

The circles and the hexagons were the additional patterns simulated on *QuickField* and then designed at the beginning of the project (see **Figure 5.6**). The different shapes of the patterns can be interesting to study not only regarding their effect on the transmission and sheet resistance but also on the flexibility. Furthermore, the patterns were arranged in a hexagonal array, which could have an impact on the crack propagation during the flexibility tests.

The random square mask was the second one designed via the *Python* interface of *Klayout*. The goal of this mask was to break the repetitive order of the squares by randomly varying the line width between $15\ \mu\text{m}$ and $11\ \mu\text{m}$ and, thus, hopefully, get rid of the diffraction pattern. Note that the mask was designed with $60\ \mu\text{m}$ squares to ensure a higher percentage of patterned areas despite the larger lines. An image of this mask can also be found in **Figure 5.6**.

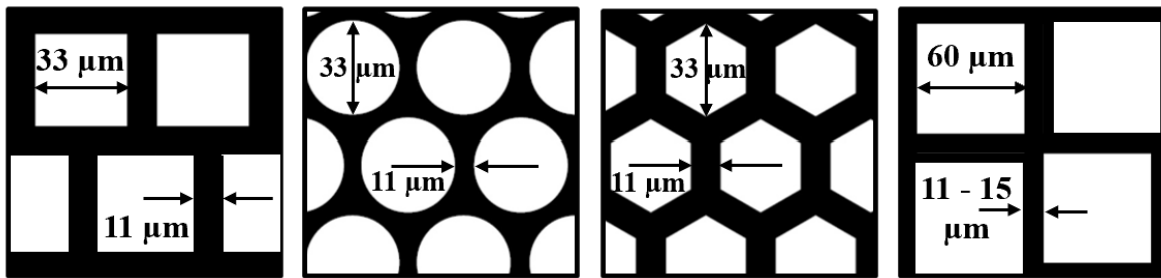


Figure 5.6: Additional mask designs with their corresponding dimensions.

Table 5.3 presents the resulting optoelectronic properties of these new designs. The electrodes were all composed of a tri-layer stack made with gold and ITO, just like the ones presented in the article. The thickness of the gold layer was optimized to maximize the transmission of the samples while keeping the sheet resistance below $50\ \Omega/\square$, and the thicknesses of the ITO layers were also optimized accordingly through *OpenFilters*. Regarding diffraction, all the patterns, including the random squares, produced a diffraction pattern. Even though the squares were more randomly placed than in the other designs, the displacement variation was simply too small to avoid generating diffraction, since it still created an overall ordered pattern.

As expected, the shifted square patterns gave similar results in terms of optoelectronic properties for the same gold thicknesses as the original square designs. Regarding the random squares, the transmission was around 2% lower than the other square design for the same square size and gold thickness. However, the random displacement of the squares made for some larger lines, reducing the quantity of patterned areas in favour of conducting areas and thus decreasing the overall transmission. Note that, during the depositions, the evaluation of the thicknesses of the layers relied on the deposition rate of the individual materials. Although reliable, this technique is more subject to generating slight variations in the thicknesses over time compared to other monitoring approaches, such as quartz crystal monitoring and *in situ* ellipsometry. Therefore, the slightly

different optoelectronic properties observed when comparing same-sized patterns can also be partially explained by this.

Table 5.3: Optoelectronic properties for the additional types of patterns with optimized gold thicknesses in an IMI stack.

Type of pattern	T at 550 nm [%]	S_T at 550 nm [%]	R_s [$\Omega/\square$]	Simulated T and R_s [% $\Omega/\square$]		Gold layer thickness [nm]
33 μm shifted squares	83.4	1.6	43.5	83.7	40	10
60 μm shifted squares	85.5	1.4	46.1	85.4	42	11
Circles	83.7	1.5	44.3	82.4	26	10
Hexagons	82.0	1.0	42.8	81.5	23	10
Random squares	83.3	1.7	39.9	-	-	11

The circles and the hexagons also showcased T_{lum} , S_T , and R_s values in the same range as the other patterns. Since they were simulated in *QuickField*, it is also possible to compare the expected values with the experimental ones, as shown in **Table 5.3**. While the transmission is close, it is possible to see that the values for the sheet resistance differ more strongly from what was expected. This can most likely be explained by the change from an orthogonal array in the simulations to a hexagonal array in the mask designs. However, no extensive study was done, since the patterns generated diffraction and had a lower luminous transmittance for similar sheet resistance compared to the square or the random line pattern.

Before examining the flexibility of the samples fabricated with the new patterns, it is valuable to mention that an additional test was performed regarding the scattering of the electrodes. In the complete device, the electrode will be placed in a medium with a n around 1.3. This differs from the refractive index of air ($n = 1$), under which the optical measurements were done. With the

alternative medium, the index contrast between the latter and the sample becomes smaller, thus potentially reducing the amount of scattering produced. Therefore, it was interesting to redo the measurements but, this time, with the samples placed in water ($n = 1.33$). Following the measurements, where the electrode was placed inside a water cell, it was found that scattering was lowered by around 50% compared to the value obtained in air. This allows more leeway in the scattering values for the electrode, as a scattering below 2% would successfully respect the 1% objective in the final device.

Testing for Flexibility

Figure 5.7 presents the flexibility results for the additional types of patterns, where each electrode was made with the IMI stack and the corresponding gold thicknesses presented in **Table 5.3**. The key results from these figures are summarized in **Table 5.4**. Note that the 60 μm shifted square sample is not presented, as it gave similar results as the 33 μm one. Additionally, the shifted squares were measured with the uninterrupted lines placed parallel and perpendicular to the bending direction. Only the latter is displayed in **Figure 5.7**, as both ways gave similar results.

Table 5.4: Key results from the flexibility tests performed on IMI tri-layer electrodes patterned with shifted and random squares as well as circles and hexagons.

Type of pattern	$d_{\min}$ with no cycles [mm]	R_s at $d = 7$ mm [$\Omega/\square$]	d and corresponding R_s after 1000 bending cycles [mm $\Omega/\square$]	
33 μm shifted squares	10	Non-conductive	14	45
Random squares	12	468	14	43
Circles	10	246	12	46
Hexagons	9	192	12	43.5

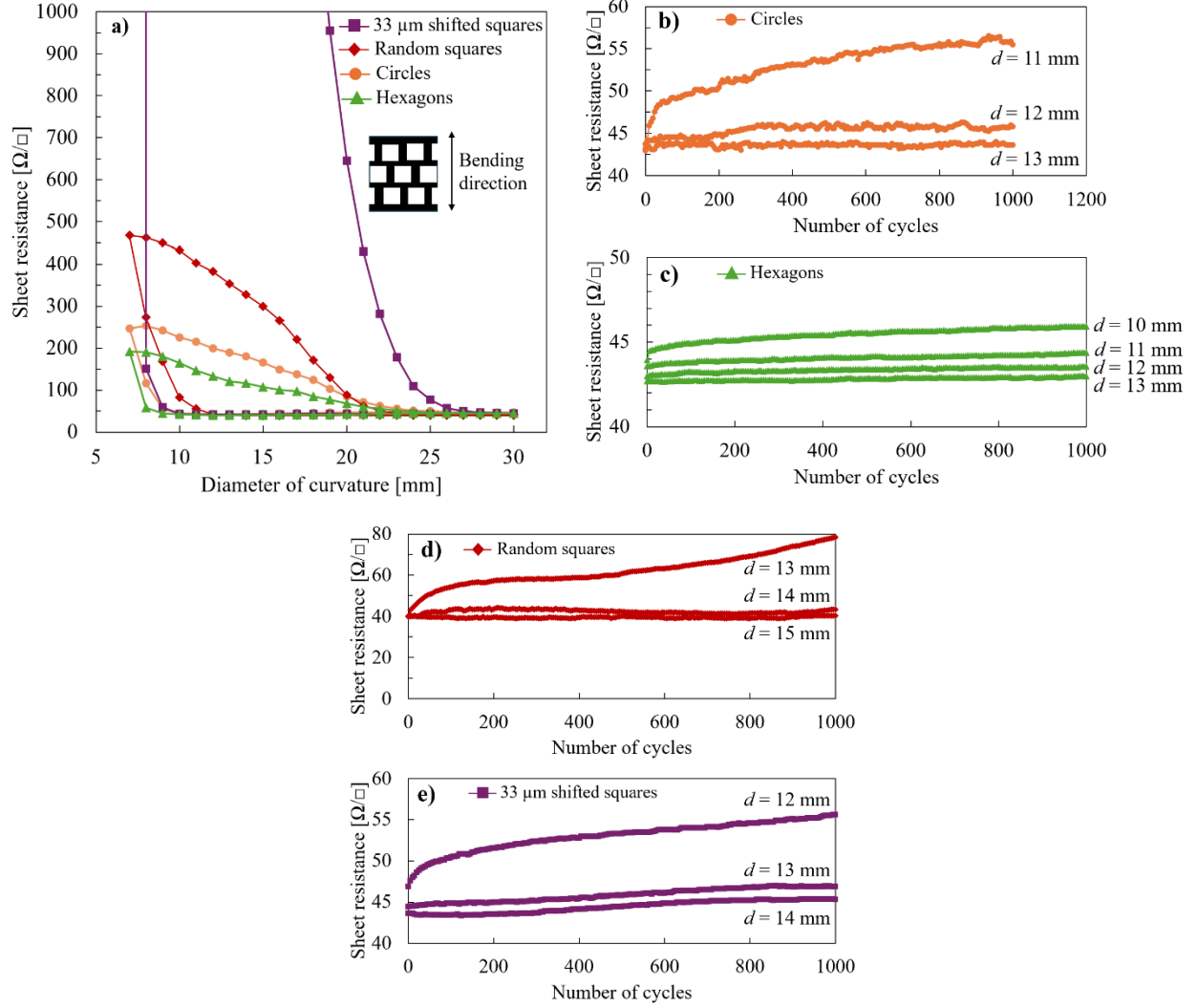


Figure 5.7: Flexibility tests for different patterned tri-layer electrodes where, a) the diameter is varied from 30 mm down to 7 mm and vice versa and, b), c), d) and e) the minimum diameter is fixed at a given d value, and 1000 bending cycles are made for each one (between d and $d + 20$ mm).

The hexagon pattern reached the lowest $d_{\min}$ at 9 mm, followed by the circles and shifted squares at $d_{\min} = 10$ mm. By comparing the latter to the standard 33 μm squares, it can be noticed that the $d_{\min}$ value was lowered by 1 mm, making the new pattern appear slightly more flexible than the original one. However, it did not prevent the sample from becoming non-conductive once it reached $d = 7$ mm. When looking at the different sheet resistance values obtained at the same $d = 7$ mm, the circles and hexagons demonstrated far superior properties than the shifted and non-shifted square designs.

As previously discussed, when looking for the presence of cracking under the microscope, it was noticed that the corners of the squares seemed to be a problematic area, which is why it comes as no surprise that rounder patterns performed far better. Indeed, the absence of sharp corners helped minimize the creation of cracks and thus improved the flexibility of the patterns, allowing the samples to remain conductive throughout the whole bending process contrarily to square patterns, shifted or not. **Figure 5.8** shows a microscope image of the IMI circle pattern bent at $d = 7$ mm. By comparing it with the first image in **Figure 5.1** (60 μm squares at $d = 7$ mm), it can be observed that the number of cracks is far less significant in the circle pattern compared to the square one. This confirms that the pattern choice indeed impacts the creation of cracks during bending tests. The hexagonal array could also have affected the overall flexibility of the sample. However, based on the results of the shifted squares, it seems that the shape of the patterns has a greater effect on flexibility than their arrangement. That being said, it can be observed that, surprisingly, the random squares also remained conductive through the various diameters of curvature. This can, most likely, be explained by the presence of thicker lines that allowed for an overall larger conductive area, which compensated more efficiently for the damaged paths.

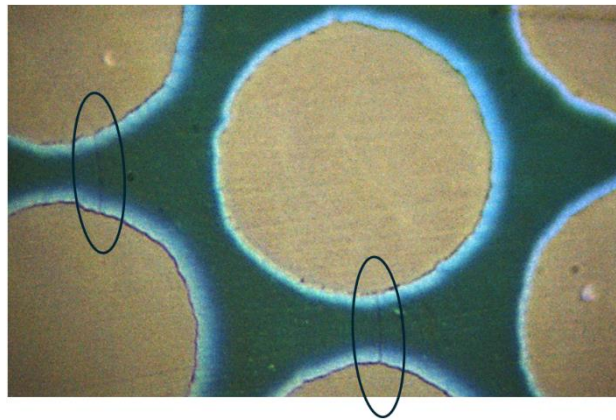


Figure 5.8: Optical microscope picture of a circle patterned ITO (43 nm)/Au (10 nm)/ITO (43 nm) sample bent at $d = 7$ mm. Dark ellipses showcase the cracks of interest.

In **Figures 5.7b**, **5.7c**, **5.7d**, and **5.7e**, the same trends presented in the article can be observed with the new masks. Indeed, for each type of pattern, the sheet resistance started increasing at a higher diameter of curvature compared to the previous test with no cycling. The hexagon and the circles had the lowest $d_{\min}$ among the new patterns at 13 mm. However, when comparing the two patterns, one can see that the sheet resistance increase is lower for the hexagons, with a $0.7 \Omega/\square$ increase

compared to $1.7 \Omega/\square$ for the circles, both at $d = 12$ mm. In addition, the circles showed fluctuations in the sheet resistance during cycling, leading us to believe that the pattern might not be ideal for multiple bending cycles. However, the reasons behind these R_s fluctuations are unclear, and further testing would be required to better understand the mechanisms at play.

When comparing the shifted squares to the normal ones, no improvements in the flexibility are observed and the $d_{\min}$ is even higher by 1 mm, showing that the new pattern did not help with the flexibility as was intended. This is most likely because the pattern did not affect the crack formation, which is made worse by the multiple cycles, as explained in Section 5.2. The random squares also did not show any marked improvement.

When comparing all the electrode designs, it can be seen that the random line design led to the best overall performance. Indeed, it avoided the generation of a diffraction pattern thanks to the random placement of the lines. Furthermore, it also allowed to obtain the highest transmission among the different samples. This is most likely due to a more ideal ratio between conductive and patterned areas, which maximized the transmission while keeping adequate sheet resistance.

Regarding the flexibility, the random lines reached the lowest $d_{\min}$ with and without cycles, with values of 13 mm and 9 mm, respectively. It is interesting to note that the hexagon pattern also gave the same results for $d_{\min}$ both with and without cycles. However, when lowering the diameter of curvature to 7 mm, with no cycles, it can be observed that the random lines stayed at a lower sheet resistance of $87 \Omega/\square$ compared to $192 \Omega/\square$ for the hexagons. Since the goal is to keep the sheet resistance as low as possible with the smallest diameter of curvature obtainable, it demonstrates that the random line pattern is the best option. This target is set so that the electrode can be used in a wide variety of applications, regardless of the required bending diameter. The better performance of the random lines can be explained by the fact that this pattern, by its nature, avoids repetitive shapes. Therefore, if a type of shape shows weakness in a particular section, for example, in the corners like for the squares or at the centre like for the circles, this weakness is not repeated over the entire surface of the electrode, thus increasing the chance of keeping a low R_s .

While the hexagons did not outperform the random lines, they showed the best flexibility among the other types of designs. This can first be explained by the absence of sharp corners, like in the square patterns, which helped minimize the number of cracks formed during bending. On the other hand, this argument would also apply to the circle pattern, which, while performing better than the

squares, showed a higher $d_{\min}$ and R_s increase than the hexagons. The reason behind this difference needs to be explored further, but a first hypothesis could be that having even lines between the patterns, compared to some larger triangular areas in the circle array, helps avoid uneven stress distribution during the bending, which could lead to more severe cracking.

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

This project aimed to develop highly transparent and flexible electrodes that would meet the target requirements set by the industrial partner, which included avoiding the presence of silver in the electrode. To achieve this objective, two techniques were combined to fabricate the final device. First, the electrode was patterned using photolithography. Then, a tri-layer stack made of ITO and gold was deposited via magnetron sputtering on top of the resist-patterned PET substrate before being placed in a microstrip remover. This lifted-off the resists, revealing the final tri-layer patterned electrode. For an adequate final product, key optimization steps had to be performed to choose the materials and their thicknesses and select the type and size of the patterns.

The addition of the ITO layers above and below the gold layer increased the overall transmission of the sample. For example, a non-patterned ITO (43 nm)/Au (10 nm)/ITO (43 nm) stack, where the ITO thicknesses were optically optimized, led to a theoretical 14.75% increase in luminous transmittance. Besides this increase, the top ITO layer provided a conductive surface for the electrode, better mechanical durability, as well as a $\sim 1 \text{ } \Omega/\square$ reduction in the sheet resistance for a 43-nm-thick layer. The ITO bottom layer, in this example being the same thickness as the top one, also lowered the sheet resistance by another $\sim 1 \text{ } \Omega/\square$, but more interestingly, it was also discovered that the ITO acted as a seed layer for the growth of the gold film, promoting an earlier percolation threshold. This phenomenon helped reduce the sheet resistance even more, bringing it down by an additional $5.4 \text{ } \Omega/\square$ in the case of the non-patterned ITO (43 nm)/Au (10 nm)/ITO (43 nm) sample. Regarding flexibility, the non-patterned tri-layer stack showed improved performance compared to a non-patterned single layer ITO sample by being able to reach a lower $d_{\min}$ (11 mm vs. 15 mm) while also maintaining a much lower sheet resistance at $d = 7 \text{ mm}$ ($19.1 \text{ } \Omega/\square$ vs. $1380 \text{ } \Omega/\square$). The same trend was also observed when the electrodes were submitted to 1000 bending cycles, demonstrating the positive impact the encapsulated gold layer can have on the flexibility of the electrode.

The patterning allowed for further improvements in the transmission and the flexibility of the electrode while keeping the sheet resistance in the targeted range. For each size and type of pattern,

the thickness of the gold layer could be optimized to give the best results in transmission while ensuring the sheet resistance stayed below $50 \Omega/\square$. Using this approach, the different pattern types and sizes gave similar results regarding optoelectronic properties. However, it was observed that the ordered designs produced diffraction patterns, which was not the case for the random lines. Regarding the flexibility, the type of pattern had a clear effect on the $d_{\min}$ and the total R_s increase, with the random lines giving the best results (equivalent or lower $d_{\min}$ and lower R_s increase among all the patterned samples).

Looking back at Sub-objective 1 as defined in Chapter 1 - Section 1.3, it is possible to compare the target values to the ones obtained with the best sample, i.e., the ITO (38 nm)/Au (20 nm)/ITO (44 nm) random line patterned electrode. First, the sheet resistance was below $50 \Omega/\square$ with a final value of $49 \Omega/\square$. On a PET substrate, the luminous transmittance of the electrode was 85%, which could be brought to 90% by using an MgF_2 backside-coated PET substrate. However, the scattering was above 1%, with 1.7% on PET and 1.8% on MgF_2 -coated PET, both at 550 nm. However, as explained in Section 5.6, these scattering values can be lowered below 1% when the electrode is placed in the complete device, thus respecting the established guideline.

Regarding flexibility, the electrode managed to reach a minimum diameter of curvature of 9 mm before showing any signs of sheet resistance increase, which is 6 mm lower than the $d_{\min}$ obtained with a non-patterned ITO-based electrode. The tri-layer randomly patterned electrode also had a much lower maximum sheet resistance at $d = 7$ mm, reaching $87 \Omega/\square$ compared to $1380 \Omega/\square$ for the non-patterned ITO-based electrode, with both samples having a starting sheet resistance in the $40 \Omega/\square$ range. Hence, we can conclude that a highly transparent and flexible electrode was developed, thus fulfilling Sub-objective 1. Specific aspects that could still be improved will be detailed in the upcoming Section 6.2.

In the case of Sub-objective 2, detailed in Section 1.3, the multiple types, sizes, and arrays of patterns tested allowed for a deeper understanding of their impact on the electrode's transmission, conductivity, and flexibility. The study also included a review of their effect on the scattering and the presence of diffraction.

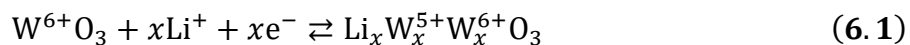
Finally, Sub-objective 3 was meant to put forward the need to develop a flexibility tool. By looking at what was done in the literature and with the help of the FCSEL technicians, a reliable flexibility tool was built to assess the flexibility of the electrodes. The tool, described in Section 3.5.3, allowed

the electrodes to bend at different diameters of curvature and permitted multiple bending cycles. The system, which was extensively used in this work, will also serve in other projects, making its fabrication a long-lasting advantage for the laboratory.

6.2 Recommendations

During the project, it was possible to see how the developed patterned tri-layer electrodes performed independently. To move forward with the project, it would be interesting to see how they hold up when implemented in a more complete device. Indeed, placing the electrodes within an electrochromic device would allow us to see if their performance remains adequate when presented with more precise constraints. This would allow us to evaluate the adaptability of the fabricated prototypes, which is an important aspect when launching a new type of electrode on the market. In addition, further tests could be done to evaluate the environmental durability of the electrodes on their own and in the electrochromic all-solid-state device, which is also a crucial characteristic of marketability.

A first step towards implementing the electrode in a complete electrochromic device was done at the end of the project when a 200 nm layer of WO₃ was deposited on top of a random line patterned tri-layer electrode. The WO₃, initially transparent, was then coloured by chronoamperometry. For this process, the fabricated electrode (working electrode) is placed in a three-electrode setup with a reference and a counter electrode and then put in an electrolyte solution. The potential applied on the working electrode is established with respect to the reference electrode, here a saturated calomel electrode, while the current flows between the working and counter electrodes. For the experiment, the electrodes were placed in an electrolyte solution of LiClO₄:PC, and a -1 V potential was applied for 60 seconds, while the current was collected on a platinum electrode serving as the counter electrode. The simultaneous insertion of Li⁺ ions and injection of electrons resulted in the coloration of the WO₃ film as per the chemical reaction presented below.



While WO_3 is colourless, explaining the original transparency of the film, Li_xWO_3 is blue, thus producing the colour change observed during the electrochemical reaction. **Figure 6.1** presents a picture of the WO_3 -coated electrode before and after the colouring process. From the picture, it is possible to see that the coloration process worked and that the colour appears uniform on the sample despite an uneven surface current due to the patterned nature of the electrode. One can also see that the patterns are slightly more visible here than in the picture presented above (see **Figure 4.7 g**). This comes from the fact that 25 nm of gold was used during the deposition (instead of 20 nm) to lower the sheet resistance to $\sim 35 \Omega/\square$, a value closer to one of the commercial ITO electrodes used in the electrochromic project. Higher sheet resistance would have most likely worked just as well, but this allowed the removal of a variable from the experimental process. Evidently, a lot more tests and characterizations need to be made to have a fully functional device, but this first experience gave very promising results and grounds to build upon.

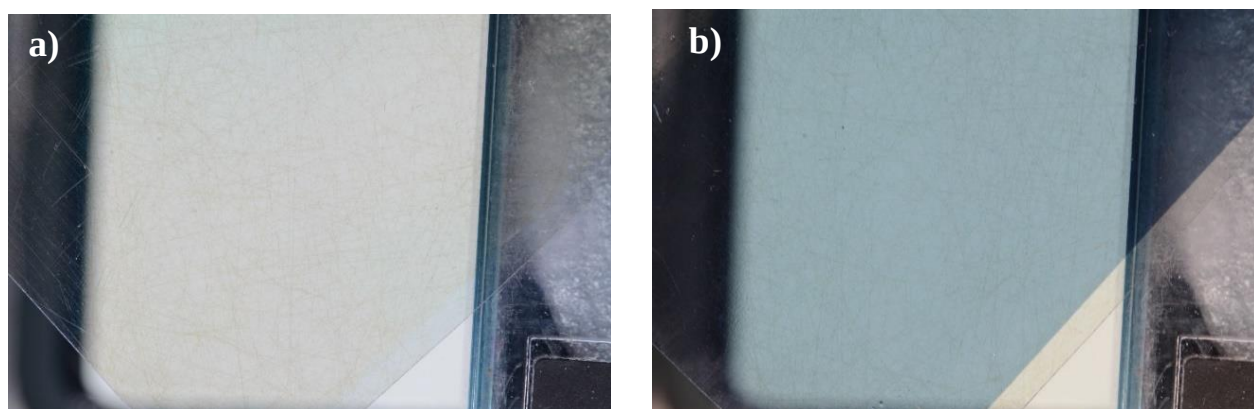


Figure 6.1: Pictures of a WO_3 -coated tri-layer random line patterned electrode a) before the electrochemical reaction (bleached state) and b) after the reaction, leading to a blue coloration of the WO_3 film (coloured state).

Regarding the fabricated electrodes, an improvement could be made in the pattern design to ideally obtain even better optoelectronic performance and flexibility. The recommendation would be to re-design some of the masks with the same types and sizes of patterns but decrease the line width. First, this could help suppress the diffraction patterns, even for non-random patterns, thus bringing back the possibility of using ordered patterns for the electrodes. Furthermore, since the patterns are kept the same size, this would also slightly increase the line density, which could help improve the overall flexibility of the samples. Additionally, the smaller line width with the same size patterns

would lead to a higher percentage of patterned area, resulting in an increase in the transmission, but also in the sheet resistance. The latter could be minimized by adjusting the gold thickness, which, if the lines are thin enough, would not have a marked impact on the transmission. Being able to increase the thickness of the gold layer rather than trying to minimize it would also be easier, since, as discussed in Section 4.2.3.2, thin gold films become discontinuous and thus non-conductive below a threshold thickness. A thicker gold layer could also potentially help with the overall flexibility of the sample.

Keeping to the subject of the flexibility of the electrodes, the tool developed to test this characteristic, although very reliable and efficient, only measures it along one axis of the electrode. For specific applications, including in the eyewear industry, it could also be interesting to assess the flexibility of the electrode when stress is applied in both the x and y axes simultaneously. This would lead to a study on the flexibility, but also on what could be called the deformability of the electrode. However, this requires developing another flexibility tool, which could be an interesting sub-objective in a future project. **Figure 6.2** shows a schematic of the principles that a tool could use to measure the deformability of the electrode.

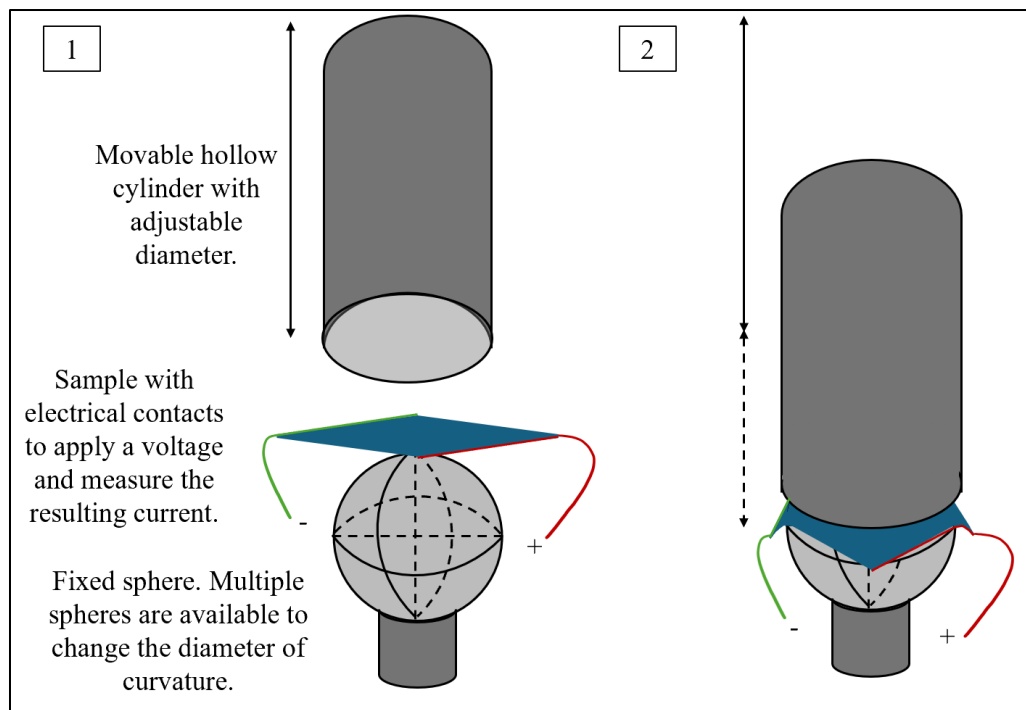


Figure 6.2: Simplified schematic of a system that could measure the deformability of an electrode.

Finally, another project could also be led in parallel to the presented one, which would focus on the flexibility of ITO itself. Indeed, it is well known that by adjusting the deposition conditions, one can improve the optoelectronic properties of the ITO film. However, the impact those conditions have on the flexibility of ITO is much less studied. During the project, it was noticed that our lab-deposited ITO seemed to have higher flexibility than the ones shown in the different articles, leading us to believe that the deposition conditions influenced the flexibility. To test this theory further, flexibility tests were performed with 120 nm ITO films deposited under various deposition conditions, more precisely, different reactive gas proportions. The results of these first tests lean towards the initial hypothesis, namely that the deposition conditions have a marked impact on the flexibility of the ITO, as the pure argon sample showed a higher resistance increase compared to the ITO deposited with added O_2 or H_2 . In the same vein, a study of the impact of low-temperature annealing or flash lamp annealing could also be done to see if it affects the brittleness of the ITO. Even though it is not directly related to the fabrication of electrodes, it could still be valuable knowledge, since it could allow for improvements in the flexibility of the presented electrodes or any other devices that use ITO as one of their constituent materials.

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