Piezoresistive response of nano-architectured Ti_xCu_y thin films for sensor applications

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Abstract: The present work reports on the development of piezoresistive Ti_xCu_y thin films, deposited on polymeric substrates (PET). The general idea was to analyse the influence of the Cu concentration on the signal response of the Ti-based transducers, exploring the possibility to use this thin film system as force and deformation sensors in biomedical sensing devices. The *GL*ancing *A*ngle *D*eposition, GLAD, technique was used to change the typical normal columnar growth microstructure into inclined (zigzag-like) architectures, aiming to tune the mechanical and electrical responses of the thin films, which may offer unique opportunities for several sensing devices. Inclined (zigzag grown) thin films were prepared with increasing amounts of Cu and characterized in terms of the most relevant properties for sensing applications. The piezoresistive response was analyzed trough the evaluation of the Gauge Factor, K. The incident angles of the particle flux α = 45º were used to prepare the nano-architectured zigzag Ti_xCu_y thin films. The Gauge factor ranges from 1.24 ± 0.03 to 16.34±0.43 for intermetallic $Ti_{0.92}Cu_{0.08}$ and pure Cu thin films, respectively. For the deposited thin films small voids are formed and the voids density decreases considerably with increasing Cu content. Taking in account the: electrical resistance linearity, low noise and the highest K value found for Ti_xCu_y films (K= 3.6±0.1), the most promising results were obtained when the polymer was coated with a stoichiometry of$Ti_{0.37}Cu_{0.63}$. The overall set of results also show the viability of these materials to be used as piezoresistive sensors, namely in biological environments, such as catheters, needles or endoscopes with sensing capabilities.

Keywords: Piezoresistive, Gauge Factor, GLAD, Thin Films, Titanium, Copper.

1 Introduction

Developing advanced surgical tools for minimally invasive procedures represents an activity of central importance for improving human health. A key challenge relies on establishing biocompatible interfaces in different types of devices, and capable to adapt to the contours of the body. Titanium (Ti) is well-known by its biocompatibility with human tissues, corrosion resistance, strength, elasticity and excellent thermal and chemical stability [1, 2]. Furthermore, when combined with other metals, like copper (Cu), important biocompatible properties may result, such as high thermal and electrical conductivities, good ductility and tensile strength and good corrosion resistance in severe corrosive biological environments [3, 4]. On the other hand, the use of electromechanical coupling effects is becoming increasingly attractive in thin film technology, due to its possible use for strain or strain-rate measurements and in mechanical and structural monitoring [5].

About a decade ago, a very significant and reversible correlation between the mechanical deformation and the electrical resistance of single- and multi-walled carbon nanotubes was discovered [6-9]. Since then, several composite materials have been developed, including a few types of thin films. Those materials have the ability to change significantly their electrical response when subjected to strain, which is being accepted as a suitable approach for the development of high sensitive polymer-based strain sensors [10-13]. As a result of straining, some of these composite materials exhibit a fairly linear and reversible electrical resistance change [13-15]. Following a similar idea, conducting materials such as polycrystalline metals should also reveal strain sensitivity, opening new possibilities to be explored within the field of sensing applications.

An emerging and attractive method to build up strain sensing materials is being developed, focusing on the development of systems where the electrode material itself acts as sensor [16]. This is particularly challenging given the relatively high and complex mechanical solicitations that are expected in several of these mechanical-based applications, i.e., bending, elongation and torsion. In fact, any strain sensor solution must be reliable and retain reproducibility and structural integrity over its lifetime. In basic terms, the electroactive components of such a sensor should have low elastic modulus and hold ability to accommodate large strain deformations, keeping a linear electrical response. Therefore, mechanical response and electrical transport properties are certainly crucial to be controlled. The relationship between mechanical and electrical behavior becomes even more important if the materials systems are prepared as thin films, since their strain sensitivity is expected to be different from those of the bulk materials, due to size effects, lattice defects, grains boundaries and other (micro)structural features [17], which are strongly dependent on the experimental processing parameters [18-21]. In conventional Physical Vapor Deposition (PVD) techniques, the majority of the prepared films use normal incidence, leading to well-known columnar growth normal to the substrate, at room temperature, which is characterized by very thin and vertically aligned structures, with a high compactness. The set of properties obtained are commonly known as having some mechanical and tribological constrains, namely in terms of brittleness, ductility and adhesion, together with reduced possibilities in terms of cohesion and adhesion after mechanical deformation [22, 23]. In this particular aspect, the coating of polymer-based materials reveals to be a major example of high complexity.

In the past few years, several attempts have been carried out to develop relatively complex systems that could accommodate these restrictions and some thin film deposition approaches revealed promising results. In fact, it has been shown that brittle metals used as adhesion promoters will fracture at low applied strains (<1%), leading to electrical failure, while ductile charge carrying thin films such as Au, Cu or Ag, will plastically deform at relatively higher applied strains (>3%) without electrical failure [22-25]. The ability to combine good adhesion and high strength for these flexible systems is a current challenge.

In this work, the *GLancing Angle Deposition* (GLAD) technique [26] was selected in order to modify the microstructural features of the thin films, and indirectly their physical-chemical responses to strong mechanical solicitations, maintaining the functional properties [16, 27]. Keeping the substrates in motion, Fig. 1, the GLAD techniques relies on oblique angle deposition from a given sputtered particle flux, allowing the Nano-engineering of thin films with three-dimensional microstructures, and in a continuous process.

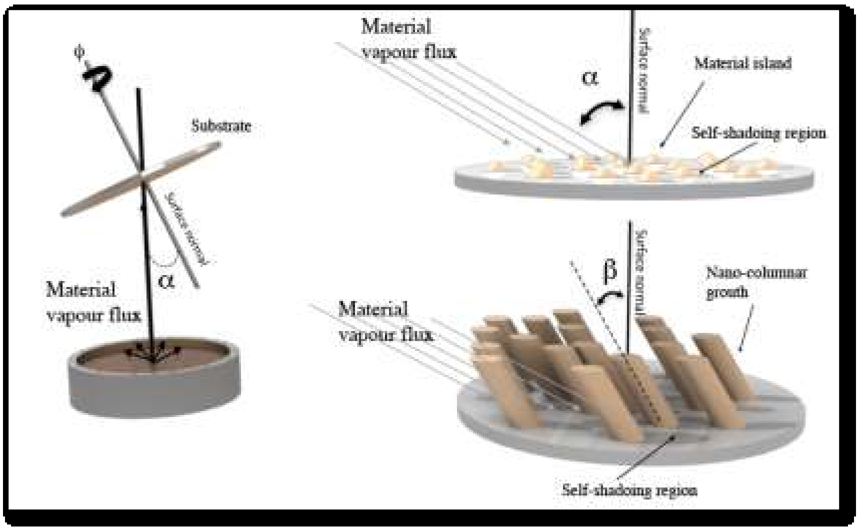


Figure 1 - Schematic representation of the GLAD system with substrate rotation in the left hand side; and representation of the effect of shadowing during the initial and subsequent stages of deposition and the control mechanism of the tilting angle of the nano-columns, on the right hand side of the figure.

In GLAD systems, the flux of sputtered (or vapored) particles impinge the substrate with a certain oblique angle, α, which enhances the atomic shadowing effect and promotes the growth of inclined columnar film microstructures, according to the angle β, Fig. 1. When the deposition flux arrives with an oblique angle at the substrate surface, an additional variable is introduced in the growth process, which has a significant influence on the development of the film's microstructure and compactness. For this purpose, the sequence for fabricating a zigzag structure, at a fixed angle, uses a stepper motor which is programmed with the following sequence: 1) grow of an oblique layer with desired thickness and angle α, without rotating the substrate; 2) rotate the substrate holder according to angle φ by 180º, at a fast rotation rate (see Fig. 1); 3) repeat steps 1 and 2 to the desired number of zigzags. Furthermore, by combining oblique incidence of the impinging sputtered particles with the motion of the substrate holder, different types of microstructural growth can be tailored among normal columns, zigzags and spirals [16, 28-31].

The results show that the electromechanical properties can be significantly changed with the different architectures produced by GLAD [16, 28, 29], allowing significant improvements in the device response and durability [32]. Taking advantage of this possibility and keeping in mind the main requirements, this research aims the development of advanced surgical tools with sensing capabilities. As a first step to reach this objective, the present work reports on an attempt to produce a Ti_xCu_y coated flexible polymeric-based sensor device, able to adapt to the irregular contours of the skin. The functionalization of the polymer, PET - Polyethylene terephthalate, was carried out by depositing different Ti_xCu_y thin films, deposited by magnetron sputtering and using the GLAD configuration. The electro-mechanical properties of the Ti_xCu_y coatings were studied in order to assess their suitability on the development of smart piezoresistive sensors.

2 Experimental

2.1 Processing of the materials

The *GLancing Angle Deposition* (GLAD) technique allows adjustment of the conventional normal columnar growth (Fig. 2a), into different columnar microstructures with specific growth architectures (Fig. 2b) [33]. This can be achieved by controlling the orientation of the substrate holder relatively to the impinging sputtered particles. For the different architectures, the β column tilt angle of the columns increases differently with the flux angle α, due to the shadowing effects between columns, among others related with the experimental details.

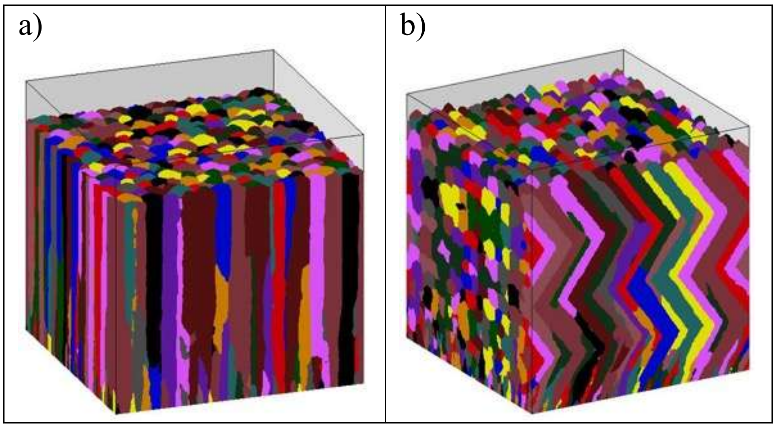


Figure 2 - Schematic representation of the thin film microstructural configurations.

In the present study, zigzag-like structures, such as those represented in Fig. 2b), were produced by varying the position of the substrate holder relatively to the target. All depositions were performed according to the parameters displayed on Table 1:

Table 1: Deposition parameters.

Zigzag Periods
2
Time (s)
2x180
Incident Flux angle, α (º)
45

Sample	**Deposition rate (nm/min**	**Final thickness (nm)**
Ti	50	300
$Ti_{77}Cu_{23}$	43	258
$Ti_{49}Cu_{51}$	45	270
$Ti_{37}Cu_{63}$	47	282
Cu	77	460

A set of Ti_xCu_y thin films was deposited onto glass and polymer substrates (PET) by DC magnetron sputtering. Prior to the depositions, the samples were sputter-cleaned, in order to promote adhesion of functional thin films without any degradation of the polymer's base properties (chemical, structural or even mechanical ones) [34, 35], a plasma reactor (Plasma System Zepto commercialized by Diener electronic), equipped with a 40 kHz/100Wgenerator and a 2.6 dm^3 volume chamber, where used for activation/functionalization of the polymeric surfaces. Plasma treatments were carried out in a pure Ar atmosphere, during 900 s. The power was set to 90 W and the work pressure was approximately 80 Pa. The depositions of the Ti_xCu_y films were performed in pure Ar plasma, using a homemade magnetron sputtering deposition system. The reactive chamber (60 dm^3 of volume), equipped with a rectangular planar and water cooled magnetron, was evacuated with a turbomolecular pump, backed by a mechanical pump, in order to obtain a base pressure below 4.0×10^{-4} Pa and to minimize the presence of oxygen in the films. The Ar (working) pressure was kept constant at 3.0×10^{-1} Pa for all depositions. The films were deposited onto grounded substrates positioned at 110 mm from the magnetron at room temperature. A DC current density of 75 A m^{-2} was applied to a titanium target (99.96 at.% purity), with $200\times100\times6$ mm^3 dimensions. The Ti target was modified with different amounts of Cu pellets (with individual area of ~ 0.196 cm^2), symmetrically distributed along the preferential erosion area, in order to change the Cu content in the coatings. The discharge parameters (target potential, applied current and working pressure) were monitored during the depositions, using a Data Acquisition/Switch Unit Agilent 34970A, equipped with a multifunction module (334907A). This unit used a RS-232 interface, and the data were acquired with a Benchlink Data Logger III software.

2.2 Sample characterization

The morphological features of the Ti_xCu_y thin films were probed by Ultra-high resolution field-emission Scanning Electron Microscope (SEM). Cross-section micrographs were obtained in a FEI Quanta 400FEG ESEM apparatus, operating at 15 keV. Rutherford Backscattering Spectrometry (RBS) technique was used to measure the atomic composition of the as-deposited samples using a 1.5 or 2 MeV ^4He beam, at normal incidence, in a small (RBS) chamber of the IST/LATR 2.5 MeV Van der Graaf accelerator. There were three detectors in the chamber: one Si surface barrier detector located at a 140° scattering angle (detector 2), and two pin-diode detectors (detectors 1 and 3) located symmetrical to each other, both at 165° (detector 3 on same side as detector 2). The composition profiles for the as-deposited samples were determined using the software NDF, after three different measurements for each sample. The resolution in the determination of atomic concentration of each sample was about 3 at.%. Further information can be found elsewhere [30]. The electrical conductivity of Ti_xCu_y thin films was measured at room temperature, using the four-point probe method in van der Pauw configuration [36, 37]. The measurements were carried out in a custom-made dark chamber. The error associated to the electrical measurements is below 1%. Beyond the conventional conductivity measurements, the piezoresistive response of the films, quantitatively analysed by the gauge factor (K) [15, 38] was also monitored in order to scan the possibilities of using these films in sensor-based applications, namely those of force/pressure and deformation transducers. In this work, electromechanical tests on the Ti_xCu_y thin films, deposited on PET substrates, were performed. The general idea was to analyse the Cu concentration and the microstructure of the deposited films (with variable number of Cu pellets), and the influence of both features on the signal response of the Ti-based transducers. For this purpose, all Ti_xCu_y thin films were coated with a two parallel rectangular Au electrodes of 2 mm length, 4 mm width and 1 mm separation. The change of the electrical resistance of the samples (approximate dimensions: $80\times4\times2$ mm^3) was measured through Au electrodes deposited on one side of the samples with a Polaron SC502 sputter, using an Agilent 34401A multimeter. The measurements were performed during the mechanical deformation of the sample, carried out with a universal testing machine from Shimadzu (model AG-IS, with a load cell of 500 N). For the 4-point-bending measurements, the Au electrodes (area of 4×1 mm^2) were deposited on the opposite face of the applied force, Fig. 3. For all experiments, 4 loading-unloading cycles were performed and the average electromechanical response was evaluated. With the aim of ensuring that the deformations of the samples are in the elastic mechanical region, the resistance was measured when the z-displacement changed from 0 to 0.4 mm. All these experiments were carried out at room temperature.

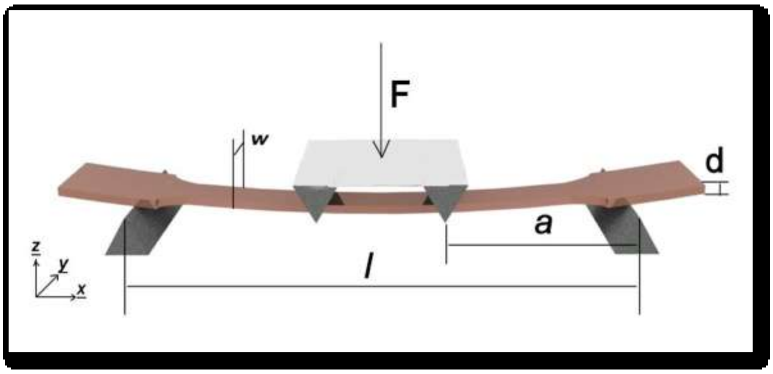


Figure 3 - Representation of the 4-point bending tests apparatus, where *d* is the thickness of the specimen (film + substrate), w the width, *a* the distance between the first and the second bending points or the third and the fourth bending points (15 mm) and *l* the distance between the first and the second lower bending points. The electrodes are placed at the center of the sample.

As mentioned above, the sensitivity of a piezoresistive sensor can be quantified through the gauge factor (K), which is defined as the relative change in electrical resistance due to an applied mechanical deformation [38]:

$$K = \frac{\Delta R/R}{\varepsilon} \tag{1}$$

where R is the initial electrical resistance of the material (Ω) and ΔR is the change in the resistance (Ω) due to the strain $\varepsilon = \frac{3dz}{5a^2}$ [38]. The change of resistance shows contributions from the geometric deformation $(1 + 2\upsilon)$, where υ is the Poisson ratio, and from the intrinsic resistivity change $\left(\frac{\Delta\rho/\rho}{\varepsilon}\right)$, allowing Equation (1) to be expressed as [38]:

$$K = \frac{\Delta\rho/\rho}{\varepsilon} + (1 + 2\upsilon) \tag{2}$$

where $\Delta\rho$ is the resistivity change due to z-displacement = 4 mm (Ω) and ρ the resistivity without any bending (Ω). The estimated Poisson's ratios for Cu ranges from 0.18 to 0.24 [39] and about 0.32 for Ti [40], which means that the geometric effect contribution to *K* is around 1.36 to 1.48 for Cu and 1.64 for Ti.

3 Results and discussion

3.1 *Chemical composition and electrical conductivity*

Aiming to the targeted force and deformation sensing applications, a set of Ti_xCu_y thin films, with different amounts of Cu, were deposited on PET substrates in order to tailor their gauge factor value.

Figure 4 shows: a) the atomic concentration (at.%) of Cu and Ti elements as a function of the Cu exposed area on the Ti target surface and; b) the evolution of the electrical conductivity with the increase of Cu content in the films.

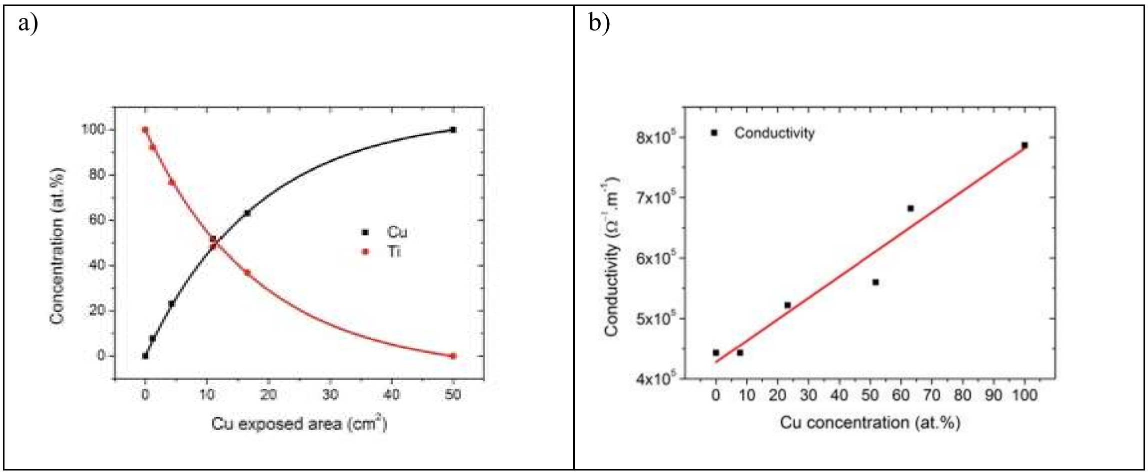


Figure 4 - a) Atomic concentration of Ti and Cu and b) electrical conductivity of the Ti_xCu_y films, a function of the Cu pellets area exposed in the Ti target.

As expected, the results show that the Cu concentration in the films increases with the area of Cu pellets placed on the surface of the Ti target, Figure 4a). In recent works developed by the authors [30], structural analyses performed by XRD-diffraction, showed evidences that for Cu contents up to about 20 at.% (Cu exposed areas varying from 1 to 5 cm^2) the films tend to develop a α-Ti(Cu) solid solution structure, where Cu act as the solute/dopant into the Ti matrix. In the same way, for Cu exposed areas above 11 cm^2, the atomic content increases from 50 at.% to 63 at.%, and the formation of amorphous Ti-Cu intermetallic phases cannot be neglected, which in fact is in accordance with the Ti-Cu phase diagram for these specific chemical compositions [41]. The particular nature of the intermetallic phases is of particular importance in the Ti_xCu_y electrical and mechanical response, as it will be shown later is this text. For the films prepared with the highest Cu content (63.1 at.%), the precipitation of the Ti-Cu intermetallic phases plus the possibility of formation of a Cu(Ti) metastable phase cannot be disregarded, since the authors found a diffraction peak near the Cu (111) orientation for samples produced with similar chemical compositions [32]. As a general trend, and taking into account the atomic composition of Cu in the Ti_xCu_y films, the samples exhibited lower conductivity values (4.35×10^5 $\Omega^{-1}.m^{-1}$) for small amounts of Cu pellets, increasing to about 7.69×10^5 $\Omega^{-1}.m^{-1}$ for the pure Cu film. In the case of the zig-zag films, they seem to exhibit lower conductivities than the columnar thin films, which were estimated in about 5.88×10^7 $\Omega^{-1}.m^{-1}$ for the pure Cu film and 2.33×10^6 $\Omega^{-1}.m^{-1}$ for the pure Ti film [42, 43].

The high disordered structure of the prepared films, mainly composed by the amorphous metastable α-Ti(Cu) phases, increases the number of structural defects and hence the number of "scattering traps" for the charge carriers resulting in high resistivity values, when compared with crystalline materials [30]. It is also possible that these defects may also affect the stability of the films and might cause hysteresis effects when they are subjected to several loading and unloading cycles.

Figure 5 shows the cross-section images of the sputtered GLAD samples, grown on glass substrates. Figure 5, a) and b), exhibits the reference thin films of Ti and Cu, respectively, prepared with the GLAD technique, both revealing a zigzag-like architecture [32, 44]. The deposition rate of Ti (~ 50 nm/min), Fig. 5a) is lower than Cu (~ 77 nm/min), Fig. 5b), which is consistent with the lower sputtering yield of Ti [45].

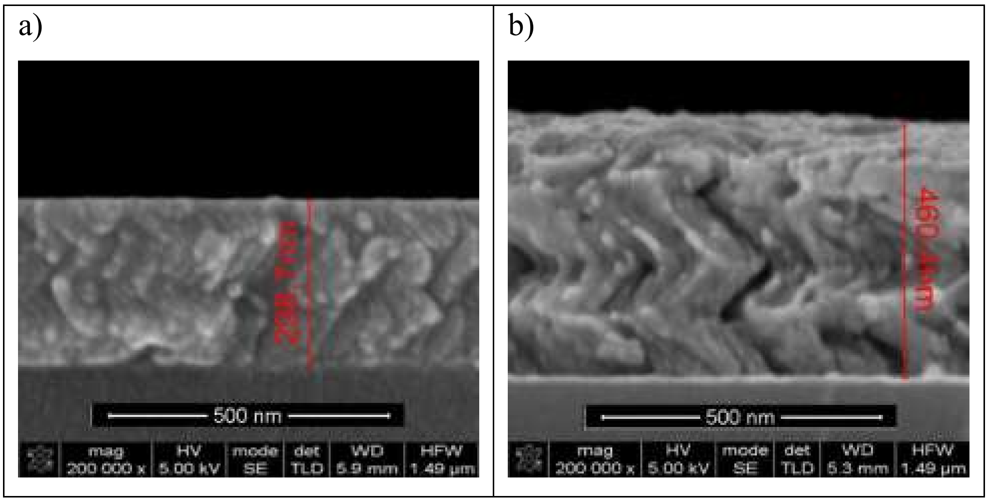


Figure 5 - SEM cross-section micrographs of the sputtered Ti and Cu samples, a) Ti with 2 zigzag periods and c) Cu with 2 zigzag periods, both with the same incident angle, α = 45°, deposited on glass substrates.

Figure 6 shows SEM micrographs taken to the surface of the Ti_xCu_y films deposited on

PET substrates, before strain experiments. It is possible to observe large voids and voids tracks aligned along the surface of the samples. For normal incidence deposition α = 0º (columnar growth), larger voids are formed and begin to elongate and evolve into well-defined void tracks. At incidence angle of α = 45º(zig-zag structures) the voids density decrease and are replaced by grain boundaries when the Cu concentration increases.

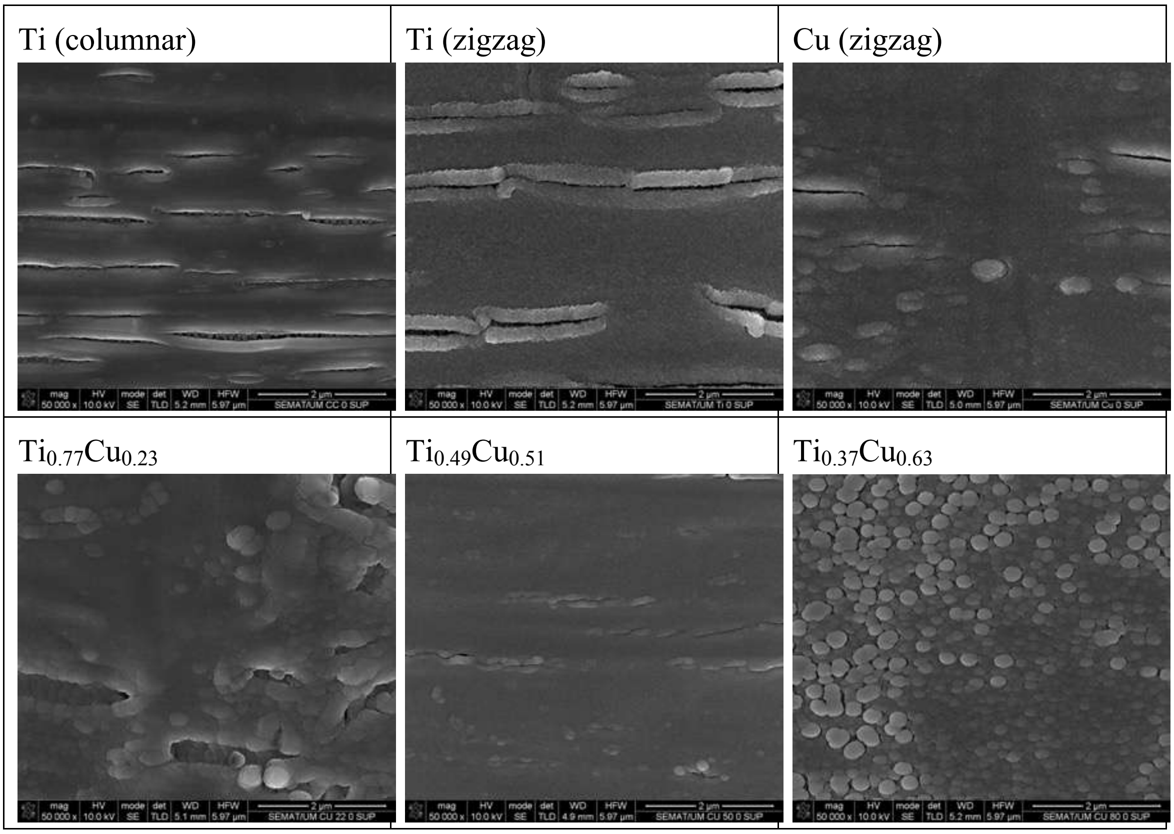

Ti (columnar)
Ti (zigzag)
Cu (zigzag)
$Ti_{0.77}Cu_{0.23}$
$Ti_{0.49}Cu_{0.51}$
$Ti_{0.37}Cu_{0.63}$

Figure 6 - SEM cross-section micrographs of the sputtered Ti, Cu, and Ti_xCu_y samples before bending, obtained on polymer substrates (PET).

The formation of voids and voids tracks is intimately related to the presence of surface depressions or surface roughness induced by the oblique angle deposition, in accordance with the works of L. Dong et. and R.W Smith et al. [46, 47]. Atoms that are being deposited in the neighbourhood of a surface depression will be attracted to the sides of the surface depression, due to the normal atomic interactions. As a result of these interactions, the sides of the surface depressions develop bumps, which shadow the regions of the surface depression below. Eventually, these bumps grow into bridges over the surface depression. If these bridges are formed below the top edge of the surface depressions (as it is common), then a surface depression remains, and a new empty space can form above the one that just pinched off at an angle consistent with the one made between the elongated surface depression and the substrate normal. This effect leads to align voids into void tracks, and explains why the orientation of the elongated voids is the same as the orientation of the void tracks. These results induce variations in the grain boundaries and porosity, which will have an effect on decreasing the probability of the electron conduction [32], and thus affecting the electrical conductivity of the as- deposited films. All these changes will be analysed in detail in section 3.2. As a result, SEM observations in Fig. 6 indicate a significant effect of the Cu addition into the pure Ti films. In fact, even for small additions of Cu, the amount of voids in the films decreased significantly, which in fact seem to disappear completely.

3.2 *Electromechanical response*

In order to quantify the piezoresistive response, dynamic measurements were performed to determine quantitative information about the sensitivity of the thin films as transducers. For sensing applications, the ability of the electrical resistance return to the initial value after bending is essential. On the other hand, the fracture strain of the film can be determined when the resistance ratio deviates from the theoretical resistance ratio. The theoretical background that supports the piezoresistive effect was developed using ductile Cu films on polyimide [48, 49]. The prediction assumes that when a metal film deposited onto a polymeric substrate is stretched, its electrical resistance R increases with the length L of the film, i.e. the film deforms homogenously and the resistivity is unaffected by micro-cracks in the films [48, 49]

$$\frac{R}{R_0} = (1 + \varepsilon)^2 \tag{3}$$

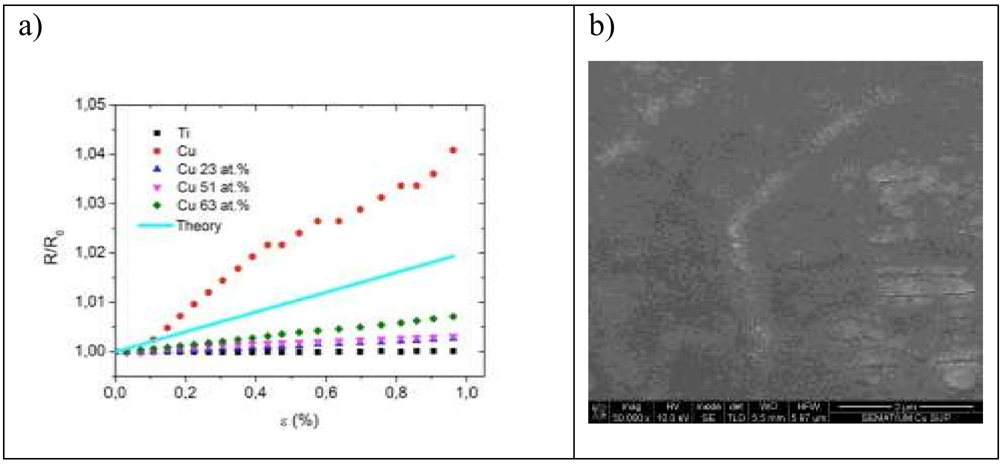
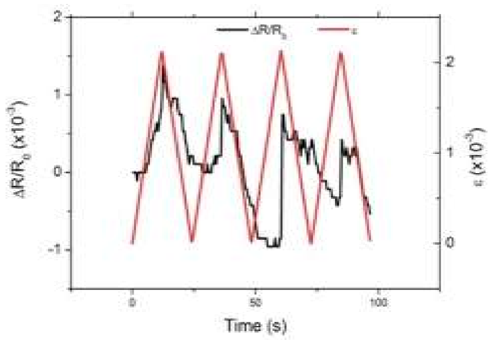
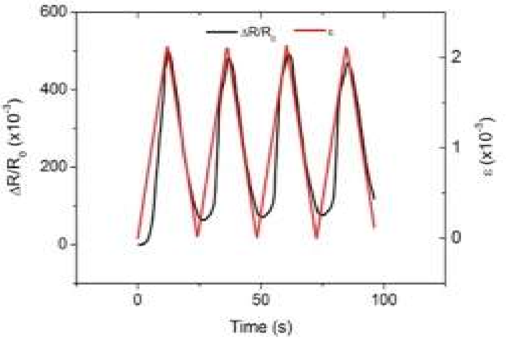


Figure 7 – a) Changes of R/R$_0$ with ε for Cu films with different Cu concentrations, b) SEM of Cu sample after bending for zigzag structures, measured on polymer substrates (PET).

Regarding the thin film system under analysis in this work, the experimental results show that when the pure Cu thin film is strained in tension, with in-situ 4-point bending resistance measurements, a sharp increase of R/R_0 appears for $\varepsilon > 0.1\%$. This trend deviates from the theoretical predictions (straight line, figure 7a), which in turn attributes the R/R_0 variation to micro–cracks formation during testing. However, this feature was not confirmed by SEM observations after repeated bending cycles, Figure 7b. Therefore, the deviation from the theoretical resistance curve must be induced by the strain sensitivity of the Cu zigzag film. Similar studies on Cu films on Kapton substrates [25], but with a thin Ti or Cr adhesion layer to improve adhesion to the substrate, indicate that the film can be plastically deformed up to 50% without any appreciable deviation from the theoretical resistance curve [25].

Despite cracks formation, a complete electrical failure did not occur for the Ti_xCu_y thin films. For the other samples (Ti and Ti_xCu_y films), the absence of the deviation of the R/R_0 vs. ε (%) curves from the theoretical one might correspond to the nonexistence of cracks formation after straining. At the initial stage ($\varepsilon < 1\%$), the changes of R/R_0 with ε follows below the theoretical relationship. Taking these trends into account, the electrical resistance changes with the applied strain ($\varepsilon < 1\%$) were also measured. Figure 8 shows the variations of the resistances ratio. $\Delta R/R_0$. and strain, ε, both as a function of time, for Ti, Cu and Ti_xCu_y zigzag films. The electrical resistance changes fairly linearly with the applied strain and this trend is maintained for the different cycles and for the different samples, except for Ti thin film.

a) Ti	b) Cu
	
c) $Ti_{0.77}Cu_{0.23}$	d) $Ti_{0.37}Cu_{0.63}$

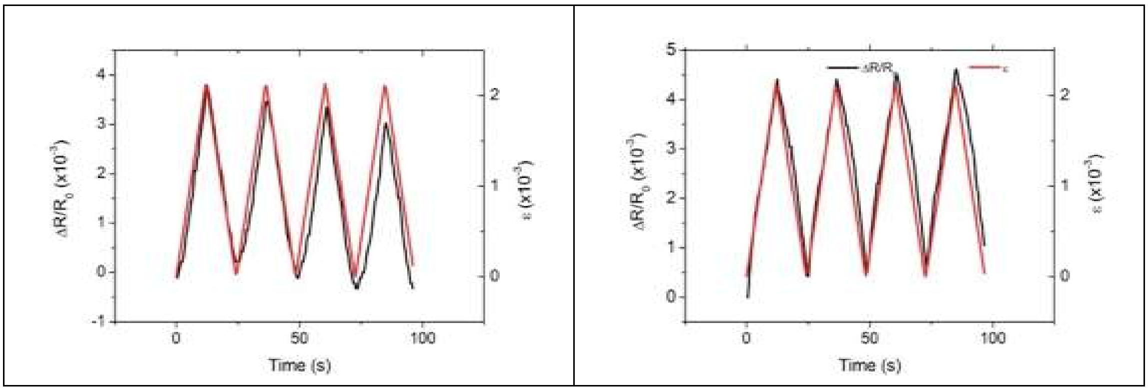


Figure 8 - Electromechanical response of samples prepared with 2 zigzag periods Ti_xCu_y films deposited on PET substrates. The z-deformation is 0.4 mm and the deformation velocity is 2 mm/min at room temperature, the incident angle is $\alpha = 45°$. a) pure Ti film; b) pure Cu film; c) $Ti_{0.77}Cu_{0.23}$ and; d) $Ti_{0.37}Cu_{0.63}$.

These results do not show any clear evidence of fracture (data not shown), which reinforces the idea of all electrically conducting materials should reveal strain sensitivity and an attractive method to build strain sensing materials. Consequently, an increase of the electrical resistance is physically understood in terms of induced strain in the local disorder of the oriented microstructure, decreasing thus the conductivity of the thin films. However, as show in figure 8a), the piezoresistive response of the Ti film shows a significant noise in the electrical response, which is progressively reduced with the increase of the Cu concentration, suggesting its relevant influence on the sensitivity. Additionally, the electromechanical response of Ti_xCu_y columnar thin films, prepared in similar experimental conditions as the ones related in Fig. 8, revealed a higher degree of noise, which in fact is very close to the behaviour of Ti zigzag thin film illustrated in Fig. 8a). This clearly demonstrates the Ti thin film inadequacy for the targeted sensor applications.

As explained before, the strain sensitivity is calculated using Eq. (2). Figure 9 shows the relative resistivity variation ΔR/R as a function of the longitudinal strain ε. The gauge factor *K*, defined previously, was extracted from the linear fits.

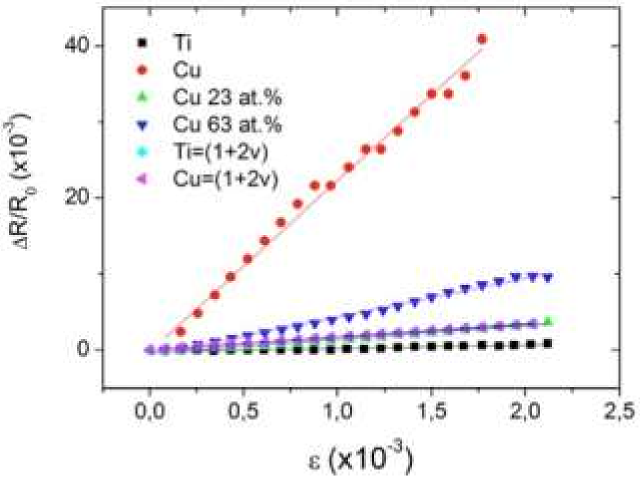


Figure 9 – Representation of the relative change in electrical resistance due to mechanical deformation, measured on polymer substrates (PET).

The slope of the linear fit with Eq. 2 (obtained with a R-square of 0.99) corresponds to the gauge factor of the sample and is presented in Table 2.

Table 2: *K* values resulting of the linear fit of $\Delta R/R_0$ as function of stress for zigzag structures.

Cu (at.%)	K
0	0.53 ± 0.16
7.8	1.24 ± 0.03
23.2	1.84 ± 0.03
51.8	1.76 ± 0.03
63.1	3.58 ± 0.15
100	16.34 ± 0.43

Each point is the average of 4 measurements. The small standard deviations associated to the calculated K values suggest no relevant influence of the conductivity on the sensitivity. Therefore, the values of the gauge factor obtained above (Table 2) show a strong intrinsic contribution of Cu to the sensitivity of the films, especially for Cu concentrations above 23.2 at.%, and a roughly negligible sensitivity for Cu concentration up to 7.8 at.%, in comparison with the value of found for Ti (K ~ 1.64, calculated from geometrical factors). However, from the results displayed in Fig. 8 and table 2, the most promising piezoresistive response was obtained when the polymer was coated with the intermediate $Ti_{0.37}Cu_{0.63}$ thin film. Indeed, the piezoresistive response of the $Ti_{0.37}Cu_{0.63}$ film shows low noise (Fig. 8d), higher K (3.6±0.1, Table 2) for the Ti_xCu_y films and a nearly linear electrical resistance evolution (Fig. 9). Moreover, Ti_xCu_y films exhibit hardness values in the order of 8 to 10 GPa, and elastic Modulus

(Er) close to 140 GPa, which gives some indication about an adequate mechanical behaviour, taking into account the targeted applications.

The stability of the piezoresistive response was also analyzed for the variation of the gauge factor with the number of bending cycles. Figure 10 shows the results obtained for $Ti_{0.49}Cu_{0.51}$ films, when subjected to 40 repeated loading and unloading cycles.

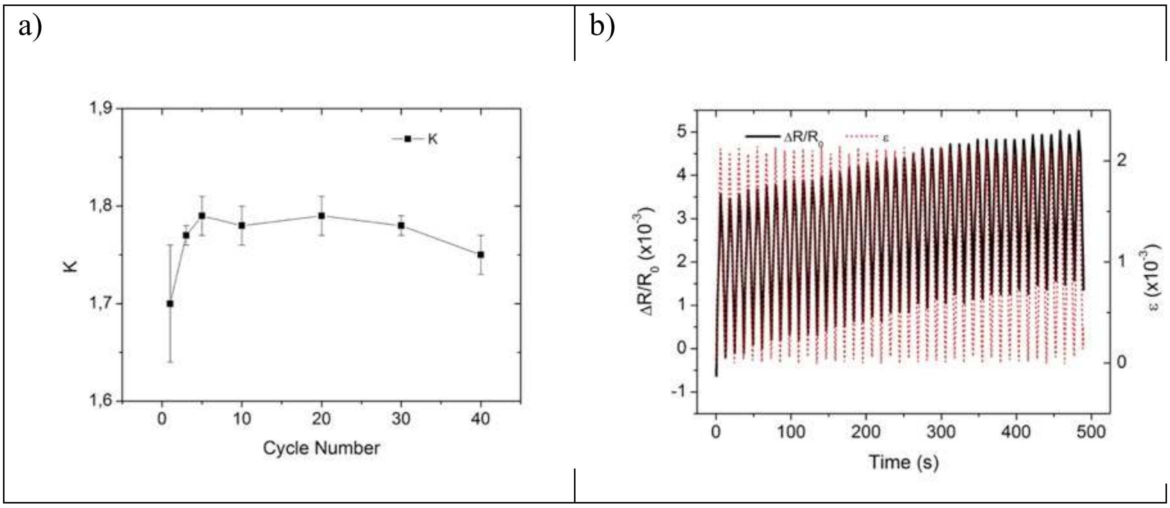


Figure 10 - Change in *K* as a function of; a) number of bending cycles, b) Sensing resistance of the $Ti_{0.49}Cu_{0.51}$ sample as a function of time during a four-point bending experiment consisting of 40 cycles with a at 0.4 mm in z-displacement, measured on polymer substrates (PET).

The plots show that after 5 cycles, the stability of the signal is demonstrated with small variations and no failure of the system was observed. For the first cycles, the gauge factor increased from 1.70 ± 0.06 to 1.80 ± 0.02, showing a tendency to stabilization along the number of cycles and with small variations (< 2.5%).

The response of the Ti_xCu_y system as a function of Cu concentration was also tested. By testing at different deformation velocities, results showed stable signals for deformation velocities between 1 mm min^{-1} and 6 mm min^{-1}, Fig. 11.

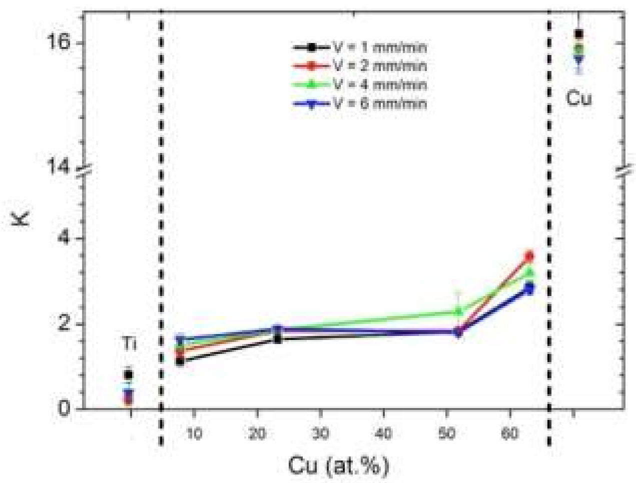


Figure 11 - Sensing of the Ti_xCu_y system for various deformation speeds, measured on polymer substrates (PET).

For this range of deformation speeds, the response time of the coating is very reproducible and linearly depends on the applied strain. The gauge factors, calculated as the ratio between the relative resistance change and the relative strain value, were found to be 0.53 ± 0.16, 1.76 ± 0.03 and 3.58 ± 0.15 for Ti, $Ti_{0.49}Cu_{0.51}$ and $Ti_{0.37}Cu_{0.63}$, respectively. For the deformation and speeds under consideration, the response time of the films is both mechanically and electrically stable. The values of the gauge factor and the linearity of the response, over a wide range of strain values, give a good indication about the viability of these materials to be used as piezoresistive sensors in biological environments.

4. Conclusion

Ti_xCu_y thin films were sputter deposited with a systematic variation of the Copper concentration in order to be tested as strain piezoresistive thin films. Upon uniaxial stretching and increasing the amount of Cu, the change in electrical conductivity of the Ti_xCu_y films induces strong variation of the response of the sensors due to their varying electrical response, which superimposes the variation of the response of the piezoresistive thin films. The best results were obtained when the polymer was coated with the intermediate $Ti_{0.37}Cu_{0.63}$ compound. The results show that the structure has a pronounced influence on the overall sensor response, leading to gauge factors up to 1.8

for the Ti_xCu_y system, and reaches a value close to 16 for the Cu thin film. However, the stability of the latter has to be further studied for potential use for sensor applications. In order to reduce even more the strain in such systems without sacrificing the electrical performance and/or changing the amplitude or period of the design, the obtained results show that the number of zigzags can be further optimized, increasing their number with several periods of smaller thickness or even with periods of various thicknesses.

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