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Deposition of Ti-Zr-O-N films by reactive magnetron sputtering of Zr target with Ti ribbons

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Abstract

In this work, we explore the addition of Ti ribbons on the racetrack of a Zr target to prepare Zr-O-N films including Ti, by reactive magnetron sputtering, with a mixture of N_2 and O_2 as reactive gases. This approach is simple and not invasive, it avoids the modification of the target and minimizes its contamination. These films were compared in terms of chemical composition, density, film growth and crystallographic structure with others prepared in identical conditions without Ti ribbons. In addition, the composition and density of the films were compared with crystallographic references from literature. The color and electrical properties of the films were evaluated as well.

It was observed that poisoning of the Zr target is promoted by the increase of the N_2+O_2 flow and the reduction of magnetron current, but it is retarded by the introduction of the Ti ribbons. This effect was particularly remarkable at lower target current, since the sputtering is confined in areas nearer to the racetrack, where the Ti ribbons are located. To account for the poisoning of the target and compare it among the different samples, a 'poisoning parameter' was defined, using a combination of the chemical composition and of the deposition rate. The color and electrical properties of the films correlate surprisingly well with the oxygen-to-metal ratio of the films, while the concentration of N does not seem to play any significant role.

Keywords: oxynitride, sputtering, titanium, zirconium, color

1. Introduction

Transition metal oxynitrides, more specifically titanium and zirconium oxynitrides, have been extensively studied. These materials are particularly interesting due to the possibility of tailoring the properties of the films (electrical, optical, mechanical) between the characteristics of a nitride (high electrical conductivity, good mechanical and tribological properties) and an oxide (excellent thermal, chemical and mechanical stability as well as high refractive index and high dielectric constant), leading to a promising functional range of materials [1–4]. In this manner, zirconium oxynitrides have been used in several applications, such as dielectric gates, temperature sensor elements, coatings for corrosion resistance [4,5], or photocatalytic material for water splitting [6], among others.

Zirconium oxynitride coatings are also particularly interesting for decorative applications [7], because the possibility of tuning the properties of the films allows to obtain a range of different intrinsic colors in the same system [4]. However, these tones are quite restricted to silver-like coatings, several shades of golden, red, brownish and blue coatings [7–9]. Additionally, only few authors quantify the evolution in the color of the films [2,7,8,10], while others reported it in a descriptive manner [11–15]. In addition, it has been previously observed that the composition of Zr-O-N films from literature was localized in a very specific region of the Zr-O-N ternary diagram [16] , which could explain the observed color restrictions.

Magnetron sputtering operated with different sources (DC, RF or pulsed-DC) has been the most used technique [5,15,17–22] to deposit Zr-O-N films. Less often, other processes such as hollow cathodic ion plating (HCIP) and filtered cathodic vacuum arc (FCVA) have also been reported [14,23]. Within this variety of deposition methods, many parameters have been explored. The used working gas is usually argon, and the reactive gases, O_2 and N_2, are

introduced separately. The N_2 concentration, in the reactive gas mixture, is typically higher. Alternatively, mixtures with fixed N_2:O_2 ratios were used. The most frequently studied parameter has been the modification of the reactive atmosphere, via variation of the N_2/O_2 ratio, or via the variation of the flow of a reactive mixture with constant composition. Regarding the chemical composition, it was observed that the majority of the reported films are located in a restricted area of the Zr-O-N composition ternary diagram, in a 'band' located around the crystalline phases ZrN, Zr_3N_4, and ZrO_2. In terms of structure, in general, the increase of the O_2 flow relatively to the N_2 flow, or the increase of O_2+N_2 mixture flow, causes a structural evolution from c-ZrN to a mixture of oxide, nitride and/or oxynitride phases, and eventually to oxide phases if the flow is high enough. In fact, the most frequently observed phases are c-ZrN, m-ZrO_2, and c-Zr_2ON_2 [15,19–21,24].

Titanium oxynitride coatings are also used in a broad range of applications such as solar collector devices [25,26], diffusion barriers [27,28], isolation films in metal-insulator-metal structures [28], wear resistance coatings [29], among others. In terms of decorative applications TiN films are known for their golden appearance [30,31], and ranges of colors from metallic grey to gold and red brownish were also reported in TiN films [32]. Regarding Ti-O-N films the colors reported in the literature are also quite restricted to metallic golden for low oxygen contents (characteristic of TiN films) and dark blue for higher oxygen contents [33,34].

Ti-O-N films are usually obtained in one of three ways: nitridation of TiO_2 [35]; oxidation of TiN [28,36] and simultaneous mixing of elements during the production, as in the case of sputtering [37,38]. Owing to the higher reactivity of oxygen compared to that of nitrogen, producing Ti-O-N by nitridation of titanium oxides can be complex. Oxidation of TiN under high oxygen partial pressure and at high temperature can result in a titanium dioxide doped with

nitrogen, TiN_xO_{2-x} which crystallizes in the anatase/rutile tetragonal structure. At low oxygen partial pressure and relatively low temperature, oxidation of titanium nitride results in a TiN–TiO solid solution, i.e. titanium oxynitride $TiN_{1-x}O_x$. which crystalizes in the cubic (NaCl) structure [37]. The simultaneous mixing of elements has been the preferred root to obtain Ti-O-N thin films.

According to literature, the used techniques for the production of Ti-O-N films is basically the same to produce Zr-O-N films. Several papers report the deposition of Ti-O-N films using magnetron sputtering with various sources (DC, RF, pulsed DC, reactive gas pulsing) using a Ti target in a gas atmosphere containing argon, nitrogen and oxygen [33,37,39–42]. Few contributions report the use nitrogen and water vapor as reactive gases [43,44]. Other methods such as Activated reactive evaporation [26] and ion plating have also been used [29]. The most studied parameter has been the modification of reactive atmosphere, via variation of the N_2/O_2 ratio. Regarding the chemical composition of the films, it was observed that the majority of them are located bellow the limit of the solid solution (line that connects TiN and TiO_2 in the Ti-O-N ternary diagram).

Regarding the structure of the films, for low oxygen flows they have a structure close to TiN with higher N/Ti ratio compared to the TiN phase. With the increase of the O_2/N_2 flow, it has been reported, for a wide range of flow, the formation of cubic TiN-TiO solid solution, with a structure close to TiN. With the increase of the oxygen flow, the peaks shift to higher angles, and the solid solution structure becomes similar to that of TiO. If the oxygen concentration is further increased, the films become amorphous and ultimately crystalize as anatase [37,39].

Although much less studied than the oxynitrides of Zr and Ti, the deposition of several intermetallic oxides (Zr-Ti-O) and nitrides (Zr-Ti-N) is reported in literature. Oxides are

generally expressed as Zr titanates, with generic formula $(Zr,Ti)O_2$ [45], although the stoichiometry and crystallography vary, e.g. $ZrTiO_4$ with monoclinic M-fergusonite structure and $(Zr,Ti)O_2$ with orthorhombic scrutinyite structure. Several phases have been also obtained via high-pressure synthesis, like the tetragonal Zr_3TiO_8 [46] or a Zr-rich titanate phase with structure that resembles an 'ordered' M-fergusonite [45].

Mixed oxides have been identified in thin films prepared with different approaches. Aita et al.[47–49] identified $(Zr,Ti)O_2$ phases with X-ray Diffraction (XRD) and Raman spectroscopy on ZrO_2-TiO_2 multilayer films prepared by RF magnetron sputtering with different thickness ratios. Li et al.[50] found mixed oxides of Ti and Zr, together with some other oxides of Ti and Mg, in TiO_2 films deposited by D.C. Magnetron Sputtering on top of a MgO-ZrO_2 coating prepared on a magnesium alloy by Plasma Electrolytic Oxidation. Monnier et al.[51] reported the formation of a Zr-Ti-O phase, likely $ZrTi_2O_6$, according to thermodynamic calculations, after the deposition of ZrO_2 by Plasma Enhanced Atomic Layer Deposition (PEALD), on a Si substrate coated with TiN by PVD. This TiN layer became slightly oxidized during the first semicycle of ALD under O_2. In this case, the presence of Zr-N bonds was not detected by X-ray photoelectron spectroscopy (XPS). Musil et al.[52] prepared Zr-Ti alloys and Zr-Ti-O films by D.C. magnetron sputtering. They reported the formation of (nano)crystalline oxides with improved cracking resistance in comparison with the metallic alloys. Pan et al. [53] studied the resistance against plasma flame ablation of ZrC-TiC coatings with different compositions prepared by vacuum plasma spray. Monoclinic ZrO_2 together with $(Zr,Ti)O_2$ were found in the film with the highest Ti concentration. That mixed oxide would be formed by the reaction of the oxides of Zr and Ti in solid and liquid states, respectively, under the high temperature of ablation (>2000ºC). Rani et al.[54] deposited Zr-Ti-O films by D.C. magnetron co-sputtering and post-annealing, and report

the formation of Zr titanate, although the O concentration evaluated by Energy Dispersive Spectroscopy (EDS) is low (ca. 13 at. %).

Films including nitrides of Zr and Ti are also reported in literature. Hodak et al. [55] have identified $Zr_{0.6}Ti_{0.4}N$ phases with (111) preferred orientation by a combination of XRD, scanning electron microscopy (SEM) and EDS in several films deposited by dual DC magnetron sputtering under different ion assistances. Pogrebnjak et al. [56,57] explored the Ti-Zr-Si-N system using computational (quantum molecular dynamics) and experimental approaches (from compound targets of Zr, Zr-Si and Zr-T-Si in N_2 atmosphere). (Zr,Ti)N phases with 111 preferred orientation were found for different chemical compositions, in agreement with the miscibility of both individual nitride phases predicted by the simulations. Jimenez et al. [58] used pulsed-DC magnetron sputtering from a target composed by TiB_2 and Zr to prepare films under different conditions of N_2 flow, bias voltage and deposition temperatures. The concentration of elements in the films was ordered as [Zr]>[B]>[Ti]. As a result, different phases were found, including (Zr,Ti)N, generally with 111 preferred orientation. Wang et al.[59] prepared Zr-Ti-N films by RF magnetron sputtering to study their application as barriers against copper diffusion. The chemical composition was $Zr_{22}Ti_{27}N_{51}$ measured by Auger Electron Spectroscopy (AES), but the presence of Ti seems to destroy the crystallinity observed in the corresponding Zr nitride film ($Zr_{30}N_{70}$). Yan et al. [60–62] deposited several Zr_xTi_yN films by multi arc ion plating using two Ti and Zr targets under different currents and N_2 flows. The films are generally richer in Zr, with $x \in$ [0.53-1.13] and $y \in$ [0.28-0.71] measured by EDS, and x>y in all of the films except one. They identified several XRD peaks which were attributed to a ZrTiN phase. Yao et al. [63] prepared Ti-Zr-N films in a closed-field unbalanced magnetron sputtering ion plating system for anti-wearing protection in cutting tools. The stoichiometry of the Zr_xTi_yN films was also richer

in Zr, with x∈[0.70-0.78] and y∈[0-0.34], and the formation of the mixed nitride phase was confirmed by XRD.

In a previous work [16,64], we explored the deposition parameter space of Zr-O-N coatings (reactive gas flow, working gas flow, target current and bias voltage) in order to reach different chemical compositions and/or increase the color palette achieved. However, the deposited films still exhibited the same chemical and color characteristics. The introduction of Ti in the Zr-O-N films was briefly studied in a previous work [65]. Therefore, the aim of this work is to explore further the formation of Zr-Ti binary oxynitrides, by the addition of titanium into the Zr-O-N system, in order to modify the properties of the abovementioned Zr-O-N films. To do so, a simple approach which consists on the location of Ti ribbons on the Zr racetrack was investigated. The Ti:Zr-O-N coatings were compared with Zr-O-N films prepared with the same deposition parameters in order to evaluate the effect of Ti addition in the properties of the films.

2. Experimental details and methods

2.1. Deposition of films

Films were deposited by reactive direct current magnetron sputtering in a laboratorial size deposition equipment onto rectangular (111) silicon (1.5 cm ×1.5 cm), glass (2.0 cm × 2.0 cm) and cylindrical mirror-polished high-speed steel substrates (Ø=3 cm, h = 0.5 cm). All the substrates were previously cleaned with alcohol and etched in a Zepto Plasma System (Diner) equipped with a 40 kHz/100 W generator. The power used was 100 W and the Ar pressure was approximately 80 Pa.

The substrates were clamped in a rotating holder (5 rpm) and placed at 75 mm from the magnetron head (Figure 1a). The base pressure was always below $2×10^{-5}$ mbar, reaching one order of magnitude lower in many cases, depending on the pumping time, while the operation

pressure was in the range of 10^{-3} mbar. The depositions were performed by sputtering of a Zr target (99.6 at.%, $10\times20\times0.6$ cm^3) using an atmosphere of Ar and a fixed mixture of N_2 and O_2 (85:15), hereafter indicated as N_2+O_2. The discharge parameters (target potential, applied current and working pressure) were monitored during the deposition using a Data Acquisition/Switch Unit Agilent 34970A, with a multifunction module. This unit uses a RS-232 interface and the data is acquired with a Benchlink Data Logger III software.

Titanium was introduced in the films by placing two Ti ribbons (only one in the case of two of the samples) over the racetrack of the zirconium target, according to the scheme depicted in Figure 1. The dimensions of the ribbons were: width: 5 mm, length: 300 mm, and thickness: 0.5 mm. The ribbons were placed above glass bases in order to electrically isolate them from the chamber and keep them at the same potential as the target. Steel pieces were adequately located to ensure the stability of the ribbons during deposition. The geometry of the frontal face and edges of the glasses (cf. Figure 1b) was machined to prevent the film deposition from connecting the ribbons to the chamber floor and leading to short circuits. This approach was preferred instead of gluing titanium pieces on the target, which is common [66], in order to avoid damaging the Zr target and prevent contaminations during future depositions.

All the films were deposited using a constant flow of Ar (25 sccm) as working gas, and different N_2+O_2 flows (2.50, 3.75, 4.00, 4.25 and 4.75 sccm). The currents applied to the Zr target, where the Ti ribbons were placed, were 1.5 and 2.0 A (7.5 and 10 mA/cm^2, respectively). In addition, the influence of the amount of titanium on the racetrack (using 1 or 2 ribbons) and the effect of substrate rotation were also studied for the film deposited at target current of 1.5 A and a flow of N_2+O_2 of 4.25 sccm. These films were compared with Zr-O-N samples deposited previously (see [16] for additional deposition details) to evaluate the effect of Ti introduction.

Therefore, the labelling of the films summarizes the synthesis conditions, using Z and TZ to indicate films deposited without and with Ti incorporation, respectively, followed by two numbers that indicates the target current (1.5 or 2.0) and the flow of reactive mixture in sccm (2.50, 3.75, 4.00, 4.25 or 4.75). Additional suffixes are used to indicate 1 Ti ribbon (1r) or 1 Ti ribbon in static mode (1rs). Therefore, the label TZ1.5-4.25-1rs indicates a film deposited with Ti, at a target current of 1.5 A, a N_2+O_2 flow of 4.25 sccm, only 1 Ti ribbon in the Zr target and no rotation. Table 1 presents all the samples included in this paper, summarizing the correlation between labeling and synthesis conditions. It is worth mentioning that not all the combinations have been studied, leading to empty cells in Table 1. The reason is that those conditions are of less interest, as it will be explained in Section 3. The deposition time of all samples was 60 min, except for the case of samples TZ2.0-4.25 and TZ1.5-4.25-1rs, which were deposited during 30 minutes. Following the same notation, the terms Z1.5, Z2.0, TZ1.5 and TZ2.0 refer to the four sets of films prepared without or with Ti at a target current of 1.5 or 2.0 A, excluding films TZ1.5-4.25-1r and TZ1.5-4.25-1rs.

2.2. Characterization of films

The morphology and thickness of the films were analyzed by scanning electron microscopy (SEM) in a FEI Quanta 400 FEG ESEM operating at 10 keV. The crystallographic structure was investigated by X-ray diffraction in grazing incidence at $\theta = 4^\circ$ on a Brucker D8 Advanced system apparatus using Cu K_α radiation (λ= 0.154 nm).

The chemical composition of the films was determined by Rutherford backscattering spectrometry (RBS), using CTN/IST Van der Graaff accelerator in an experimental chamber where three detectors were installed, one at 140º scattering angle, and two pin-diode detectors located symmetrically to each other both at 165º scattering angle. The spectra were collected for

2 MeV $^4He^+$ beam and the angle of incidence was 0º (normal incidence). The compositional profile of the samples was determined using the software IBA Data furnace NDF v9.6d [67]. The atomic and mass densities of the films were calculated from the areal density (i.e. the number of atoms in thickness in a certain area of the film, in at/cm^2) obtained from the fittings using the thicknesses and chemical compositions measured by SEM and RBS, respectively.

Optical spectrophotometry was performed using a commercial Minolta CM-2600d portable spectrophotometer (wavelength range: 360–700 nm) in order to quantify the color of the samples according to CIELab 1976 color space [68]. The diffuse and specular components of reflection of light were measured, without the UV 400 nm cut filter, and with a 3 mm aperture mask. The transparency of the films was evaluated with the method described in a previous work [64], which consists in the comparison of the color coordinates of the same film deposited on three different substrates. Therefore, opaque films show the same color coordinates in the three substrates, but these values start to deviate when the transparency of the film starts to grow.

The electrical resistivity of the conductive films deposited on glass (Figure 2, top) was measured with a Four Point Probe System composed with probes spaced by 2 mm connected to a current source DC 9818 from Time Electronics and a 2182 nanovoltmeter from Keithley, using a linear fit for the voltage current curves, the thickness of the films measured by SEM and the correction factors for finite length samples [69]. The measurement of the capacity and dielectric loss (tan$\square$) of the films deposited on steel (Figure 2 bottom) was performed with an Agilent E4980A Precision LCR Meter in the measuring frequency range of 1 kHz to 1 MHz (applied voltage of 0.5 V). Au contacts with 5 mm diameters were deposited on both sides of the samples using a Polaron SC502 sputter coater (40 nm of gold thickness). The real part of the dielectric constant was determined from the electrical capacity values considering the parallel plate

capacitor geometry, the thickness of the sample and area of the electrodes.

3. Results and discussion

The main objective of this work is to study the effect of the addition of Ti in Zr-O-N films. To do so, in Section 3.1 we will briefly summarize the characteristics observed for Zr-O-N films and their correlation with the synthesis conditions. In Section 3.2, we will perform a similar task for films including Ti, and also compare them with the samples of the Zr-O-N system. Section 3.3. is devoted to the influence of substrate rotation and the number of the Ti ribbons located on top of the Zr target. In Section 3.4 we will discuss the phases present in the films and the values of density in comparison with crystallographic references. Finally, in Section 3.5 we will study the colour and electrical properties of all films, and interpret them in terms of their characteristics and synthesis conditions.

3.1. Characteristics of the Zr-O-N films

The characteristics and properties of Zr-O-N films are summarized in Table 2. All these films (deposited at 1.5 and 2.0 A) can be sub-divided into three groups, following a sequence of common characteristics (e.g. deposition rate, chemical and crystallographic composition). The sequence starts with films Z2.0, ordered from low to high flow of N_2+O_2 (i.e. from film Z2.0-2.5 to film Z2.0-4.75), followed by Z1.5 films, also ordered from low to high flow of N_2+O_2 (i.e. from film Z1.5-3.75 to Z1.5-4.25). Following this sequence, it can be observed that the deposition rate decreases monotonically from 1.4 to 0.37 $\square$m/h (cf. Table 2 and Figure 3a and b). This behaviour corresponds to the progressive poisoning of the Zr target, and it is reflected in the characteristics of the films such as chemical composition (Figure 3a and b), crystalline phases (Figure 4a and b) and film growth (Figure 5, top rows). The chemical composition of the first group of films (Z2.0-2.5 and Z2.0-3.75) is predominantly metallic (Figure 3b), with almost no

oxygen, and a crystallographic structure corresponding to N-deficient ZrN (broad peaks in Figure 4b). In fact, sample Z2.0-2.5 shows a shift to higher angles of the peak at ca. 34º, and also a peak corresponding to metallic Zr at ca. 63º. Both films show a coarse columnar growth (Figure 5). The rest of the films show a Zr content around 40 at.%, but with a progressive decrease (from 45 to 36 at.%), and an increase of O content from 11 to 30 at.%. This causes an increase of the non-metal-to-metal (N+O)/Zr and O/Zr ratios (cf. Table 2), and a refinement of the microstructure, first with thinner columns (films Z2.0-4.0 and Z2.0-4.25), then with appearance of interrupted columns (films Z2.0-4.75, Z1.5-3.75) and finally with more compact microstructure (films Z1.5-4.0 and Z1.5-4.25). Films Z2.0-4.0 and Z2.0-4.25 show the highest N content (44 at.%), and sharp XRD peaks corresponding to ZrN. The contribution of isostructural ZrO is probably minimal, since the position of the peaks agrees very well with the ZrN standard. Film Z2.0-4.25 also shows peaks corresponding to Zr oxynitride (Zr_2ON_2) at low 2θ angles (< 35º). The remaining films (Z2.0-4.75, Z1.5-3.75, Z1.5-4.0 and Z1.5-4.25) show a quite constant N content, around 34-36 at.%, and amorphous XRD patterns, which indicates the formation of metal-poor disordered oxynitrides. These amorphous films are transparent and electrical insulators (cf. Table 2), with film Z2.0-4.75 being in the limit of opacity [64]. Since all the Z1.5 films are all very similar among them and to Z2.0-4.75, the rest of conditions of flow of reactive mixture have not been explored.

3.2. Characteristics of the Ti:Zr-O-N films

3.2.1. Overall trends of chemical composition and deposition rate

The characteristics and properties of the Ti:Zr-O-N films are summarized in Table 3. Relatively to Zr-O-N films, the addition of Ti causes the expected reduction of the Zr concentration (Figure 3), and, excepting the case of film TZ2.0-4.75, a general increase of the

metal content. The reduction of the Zr content is obviously caused by the partial coverage of the Zr target with the titanium ribbons, reducing the area of the Zr target exposed to sputtering. The increase in the total metal amount can be explained by the increased deposition rate when the films are deposited using titanium ribbons. This result is not expected, since zirconium has higher sputtering yield [70] and deposition rate than titanium (3.42 vs. 2.07 μm/h) [71].

Taking into account that the films were produced in the thermodynamic regime [16], the increase of the deposition rate may be understood by analyzing the standard enthalpies of formation of nitrides and oxides of Ti and Zr: $\Delta H_f^0(TiN) = 337.65$ kJ/mol; $\Delta H_f^0(TiO_2) = -945$ kJ/mol; $\Delta H_f^0(ZrN) = -365.26$ kJ/mol; $\Delta H_f^0(ZrO_2) = -1097.46$ kJ/mol [72,73]. The higher difficulty of Ti to form nitrides and oxides when compared with Zr, makes more complex the poisoning of the target when Ti ribbons are present. In other words, the presence of titanium would retard the passivation and oxidation of the target, observed for the Zr-O-N samples deposited in similar conditions.

In addition to the higher resistance against target poisoning when including Ti ribbons, the higher deposition rate for films with titanium can also be a consequence of the inclusion of the two titanium ribbons over the target race track. It is well known that the erosion of the target (i.e. increase of the race track depth) is accompanied by a reduction of the sputtering rate [74]. Therefore, the location of the ribbons over the racetrack of the target reduces its depth, and it would contribute to explain the higher values of deposition rate.

In contrast to the overall trend, film TZ2.0-4.75 shows a lower metal content and deposition rate than its correspondence film without Ti (Z2.0-4.75). The reason is that film TZ2.0-4.75 is the only one prepared with Ti which belongs to the group of the poisoned ones (cf. XRD patterns in Figure 4c and d, and the high value of the nonmetal-to-metal ratio (N+O)/(Zr+Ti) in Table 3).

That means that, under those deposition conditions (2.0 A and 4.75 sccm of N_2+O_2) the target is poisoned regardless of the presence of Ti ribbons (the sputtering area is larger at high current, and the influence of the presence of Ti ribbons is smaller). Therefore, in this case the deposition rate with Ti is lower, as expected considering the higher relative deposition rate of Zr vs. Ti explained before.

3.2.2. Ti:Zr-O-N films deposited at 2.0 A (TZ2.0 films)

TZ2.0 films show an increase of the O content at expenses of Zr upon the increase of N_2+O_2 flow, in agreement with what observed in the Zr-O-N series (cf. Figure 3). Both films show a relatively low concentration of Ti (10-11 at. %), and XRD patterns similar to the correspondent films without Ti (cf. Figure 4b vs. d). This is not the behaviour observed in the films deposited at 1.5 A (cf. Figure 4a vs. c). Film TZ2.0-4.25 has relatively broad peaks indexed as ZrN, whose position is slightly shifted to higher angles, probably due to the presence of Ti atoms in the matrix. Therefore, the introduction of Ti for films deposited at 2.0 A, causes a comparatively small modification of the system, which is the reason for not exploring this current for other flows of N_2+O_2.

Nevertheless, the correspondence between samples from series with and without Ti is not so simple. From a chemical composition point of view, film TZ2.0-4.75 resembles film Z1.5-4.25 (lower metal content and higher O concentration than film Z2.0-4.75). The growth mode is also similar to films of that region (Figure 5). The reason is that film TZ2.0-4.75 was produced in poisoned conditions and, as consequence, the deposition rate is lower than the correspondent film without Ti, leading to a sputtering condition with higher degree of poisoning.

An opposite observation can be made for film TZ2.0-4.25, whose chemical composition and deposition rate would resemble a film between Z2.0-3.75 and Z2.0-4.0, although much closer to

the latest one. The shape of the XRD pattern (Figure 4) and columnar growth (Figure 5) support this interpretation as well. In this case, the presence of Ti ribbons reduces the poisoning conditions of the sputtering, leading to higher deposition rates and metal content than the correspondence film without Ti (film Z2.0-4.25).

The reduction of target current from 2.0 A to 1.5 A causes an expected decrease of the overall metal content and deposition rate in both series of samples due to the reduction of the current density. The exception is the film deposited with a flow of 4.75 sccm with Ti at 1.5 A (TZ1.5-4.75), which exhibits higher metal content than the film produced with 2.0 A (cf. Figure 3). The reason for this exception is that film TZ2.0-4.75 is poisoned, which is not the case on film TZ1.5-4.75. In other words, the reduction of the magnetron current lowers the poisoning of the target. This result may be surprising, but it is because the sputtering process at 1.5 A covers a reduced sputtering area beyond the 'race track' (where the Ti ribbons are located). This means that, at lower currents, the area covered by Ti ribbons compared to the total sputtered area is proportionally much higher, and the Ti incorporation becomes a larger perturbation than at 2.0 A. As a consequence, the relative amount of Ti content increases (cf. lower values of Zr/(Zr+Ti) ratio in Table 3). In fact, the Ti content of films deposited at 1.5 A is around 20%, which is ca. double than the films deposited at 2.0 A.

3.2.3. Ti:Zr-O-N films deposited at 1.5 A (TZ1.5 films)

Overall, the trends in chemical composition when increasing the N_2+O_2 flow for TZ1.5 films are similar to TZ2.0 A, i.e. a 'poisoning effect'. To a certain extent, the TZ1.5 films behaves similarly to Z2.0 samples, but with a smaller range of variation. Taking into account that the Zr-O-N series varies from 'metallic' to 'poisoned' regimes (cf. Figure 3 and Figure 4 b vs. c), comparing some characteristics of the Z2.0 with TZ1.5 groups of samples when the N_2+O_2 flow

increases, it is observed that it seems to happen a twofold behaviour, below and above the mixture flow 4.0 sccm:

- Metal content and non-metal/metal ratio: below 4.0 sccm, the variation of the metal content exhibits a negative slope (-24.7 at.%/sccm for Z2.0 films and -4.7 at.%/sccm for TZ1.5 films). The reduction of the metal content is less pronounced in the TZ1.5 group, because of the lower target current. For flow $\geq$4.0 sccm, both groups stabilize the metal content at around 45$\pm$2 at.%. Looking to the perspective of the non-metal/metal ratio, it increases in both groups until a limit of 1.2$\pm$0.1. Unless for the metallic films, with low ratios (0.2 and 0.5), all the films exhibit non-metal/metal $\geq$1.0. The stabilization of this ratio at 1.2 is closer to the MeN stoichiometry (typically a fcc structure in the case of ZrN and TiN) relatively to the MeO_2 stoichiometry. This observation is not surprising because the N content is always higher than O content;

- O content: in the limits of the described deposition parameters, it is observed that the O content increases until it reaches 17$\pm$2 at.% in both groups. For the TZ1.5 films that value is reached when the mixture flow is 4.0 sccm, and remains stable above that flow. In the case of Z2.0 films, this concentration is reached only for the highest flow (4.75 sccm). In the case of these latter films, the higher target current justifies this observation. Only when the flow is maximum, the amount of O_2 in the working atmosphere is enough to reach the concentration of O around 17 at.%. It should be referred that only traces of oxygen (~1 at.%) were detected in the most metallic films of the Z2.0 group (Z2.0 2.5 and Z2.0-3.75);

- N content: it is surprisingly similar for all the films (34-44 at.%), except those considered more 'metallic' (Z2.0-2.5 and Z2.0-3.75, with values of 17 and 31 at.%, respectively). In the case of TZ1.5 films, the N concentration is very constant for all of them (38-40 at.%). The

working atmosphere has a N_2 partial pressure around 5.7 times higher than the one of O_2, which explains that the N concentration in the films is always higher than the one of oxygen, despite the higher affinity between the metals and oxygen;

- $Zr/(Zr+Ti)$ ratio: in the case of TZ1.5 films, the metal ratio $Zr/(Zr+Ti)$ stays very constant, ranging from 0.5 to 0.7. This is expected according to what it was referred about the deposition geometry, particularly the target-ribbons system;

- Deposition rate: The deposition rate of the TZ1.5 group is obviously lower that the one of the Z2.0 group, because of the lower target current. Below 4.0 sccm, the deposition rate decreases in both sets, but with different slopes (-385 and -225 nm·h^{-1}sccm^{-1}, for Z2.0 and TZ1.5 groups, respectively). Above 4.0 sccm, the slopes of both trends increase to -251 and 161 nm·h^{-1}sccm^{-1} for Z2.0 and TZ1.5 groups, respectively. The first value is close to the one of the TZ1.5 group below 4.0 sccm (-225 nm·h^{-1}sccm^{-1}), while surprisingly the second is positive, which is a consequence of the deposition rate of film TZ1.5-4.75.

- All these films (both groups) show a similar compact growth with interrupted columns (Figure 5).

Films TZ1.5 are significantly different from films Z1.5, which belong to the group of the poisoned ones (cf. Figure 4a vs. c). This latter group shows an O concentration of ca. 10 at.% higher than the former (24-30 vs. 14-19 at.%), and a lower metal concentration. These facts support that the application of Ti ribbons retards the poisoning of the target, in line with what was explained before. Therefore, the enhanced crystallinity of the Ti:Zr-O-N films (Figure 4c) can be related to an easier formation of Ti-N-O phases than Zr-O-N phases, which led to a more amorphous-like structural state. In fact, the XRD patterns of the TZ1.5 films are much closer to TZ2.0-4.25 than TZ2.0-4.75 (i.e. closer to the film deposited at 2.0 A with lower flow of reactive

gas, which corresponds to a lower poisoning of the target). This is opposite to what observed in Zr-O-N films, where the patterns of Z1.5 samples resemble the structures observed at 2.0 A with the highest flow of reactive mixture (i.e. more poisoned). Therefore, at 1.5 A, the Ti-containing samples are likely deposited in reactive mode, while the Zr-O-N films were already prepared in poisoned regime.

For the TZ1.5 films (Figure 4c), two regions can be distinguished depending on the N_2+O_2 flow. The first region would be formed by the films deposited with 2.50 and 3.75 sccm of N_2+O_2, and the second region englobes the coatings deposited with flows of 4.00, 4.25 and 4.75 sccm. The first group is characterized by the presence of Zr-O-N peaks (ca. 34º), together with a second contribution of TiN. In this group, the position of the peaks is slightly displaced to lower angles with respect to the references. In the second group, the diffractograms can basically be interpreted as TiN, although for lower flows of N_2+O_2 flows (4.00 and 4.25 sccm), a broad contribution of Zr-O-N can be still detected (ca. 56º), which disappears at 4.75 sccm of N_2+O_2 flow. These observations can be explained together with the evolution of chemical composition (cf. Figure 3c). It is seen that the overall metal content decreases at the expense of the O content (which corresponds to the films of the first group, where Zr-O-N phases are clearly present), until a 'steady state' is reached from 4 sccm of the reactive mixture (which would constitute the films of the second group, where the Zr-O-N phases are difficult to detect).

The effect of the increase of target current in the observed XRD patterns of the Ti:Zr-O-N films (Figure 4c to d) can be explained in terms of the replacement of Ti by Zr atoms. For both couples of films that can be compared (4.25 and 4.75 sccm N_2+O_2), the films go from reasonably well-formed TiN phases to Zr-based phases that are quite different. At 4.75 sccm, an amorphous film with high concentration of N and O is obtained (poisoned condition). In contrast, at 4.25

sccm, a coating characterized by better formed Zr-O-N phases is reached, probably doped with Ti, since the peaks are slightly displaced to high angles.

3.2.4.   Overall behavior and Poisoning Parameter.

The whole behaviour of the Zr-O-N and Ti:Zr-O-N can be sketched with the definition of a 'Poisoning Parameter (PP)', which would indicate the degree of poisoning of each condition. That parameter has to be proportional to the concentration of oxygen in the films, and inversely proportional to the concentration of metals in the films and to the deposition rate. Therefore, PP would be defined as:

$$PP = \frac{[O]}{[Zr]+k[Ti]} \cdot \frac{1}{t}$$

where *t* is the relative deposition rate (dimensionless), which is the result of the division of the deposition rate of the film by the deposition rate of the most 'metallic' film (Z2.0-2.5), and *k* a non-dimensional parameter that represents the enhanced difficulty of poisoning when Ti is present. To reach a threshold separating poisoned and non-poisoned films, such parameter has been set to 4. It is worth mentioning that the concentration of N does not play any role in the definition of this parameter, which is adequate considering its limited variation among different films (all films in the range of 34-44 at.% except metallic films Z2.0-2.5 and Z2.0-3.75).

Figure 6 shows the variation of the Poisoning Parameter for the 4 sets of samples discussed so far. It can be seen that we can define a threshold at PP=0.7, over which all films are poisoned. In general, all the sets show increased values of PP for higher values of N_2+O_2 flow, but the range of variation for Zr-O-N films deposited at 2.0 A is larger than for Ti:Zr-O-N films at 1.5 A, in agreement with what was described above. The series of Zr-O-N films (in red) can be interpreted as one (connected with a dashed line) in agreement with what was explained in Section 3.1, showing a continuous growth of PP for higher values of N_2+O_2 and lower target current. Both

samples deposited with Ti at 2.0 A show opposite behaviours, as explained before. Therefore, the film deposited at 4.25 sccm (TZ2.0-4.25) has a lower PP than the correspondent films of the other series: without Ti at 2.0 A (Z2.0-4.25) and with Ti at 1.5 A (TZ1.5-4.25). The presence of Ti contributes to reduce the poisoning observed in the former case (film Z2.0-4.25), and the higher current used than the latter (TZ1.5-4.25) leads to higher deposition rate and lower poisoning. In contrast, the film deposited at 4.75 sccm (TZ2.0-4.75) has higher value of PP than the correspondent films of the other series: without Ti 2.0 A (Z2.0-4.75) and with Ti at 1.5 A (TZ1.5-4.75). In the former case (Z2.0-4.75), both films are poisoned, but the deposition rate of the film with Ti is lower because of the lower sputtering yield of Ti relatively to Zr. In the latter case (Z1.5-4.75), the poisoning is prevented due to the higher presence of Ti in the film, which is caused by the restricted area of sputtering around the Ti ribbons. In fact, this effect is what causes that none of the Ti:Zr-O-N films shows poisoning when deposited at a target current of 1.5 A.

3.3. Influence of substrate rotation and number of Ti ribbons

Figures 7, 8 and 9 show the influence of the number of Ti ribbons and substrate rotation on the chemical composition, XRD structure and growth of the Ti:Zr-O-N films, respectively. As expected, the removal of one Ti ribbon from the Zr target leads to the reduction of the Ti concentration in the films to approximately half of the previous concentration, although the total amount of metal in the films remains unchanged. This is just related with the exposure of an area of the Zr target that was previously hidden behind the Ti ribbon, and therefore these concentrations remained unchanged when the substrate rotation is turned off. In these films, the O content is slightly reduced at expenses of N, as opposite to the O enrichment observed by previous studies [75]. Finally, when both Ti ribbons are removed, the total metal content

decreases while the Zr concentration increases slightly (from 32 to 36 at.%), and the O concentration almost doubles, from 17 to 30 at.%. This film is one of the 'poisoned' ones (cf. Figure 8, top), which highlights again the importance of the presence of Ti ribbons to avoid the poisoning of the films.

The variation of the O content is likely connected to the deposition rate. In the case of the film grown without rotation, the deposition rate increases by a factor of 4, since the substrate is continuously exposed to the target. The slight reduction of oxygen concentration (from 17 to 14 at.%) is probably a consequence of the lack of travel through the 'shadow zone' (i.e. where no deposition takes place) due to the elimination of the rotation, which reduces the absorption of gas molecules in the film surface.

At first sight, the other three samples show a contradictory behaviour, since the removal of 1 Ti ribbon leads to the increase of the deposition rate from 468 to 546 nm/h, but the removal of 2 Ti ribbons (deposition of Zr-O-N) leads to a reduction to 422 nm/h. In parallel, the oxygen content of the films varies from 19 to 17 to 30 at.% for 2, 1, and 0 ribbons, respectively (cf. Tables 2 and 3 and Figure 7). The elimination of both Ti ribbons (Z1.5-4.25) leads to a poisoned sputtering condition, which entails lower deposition rate and higher oxygen content. In contrast, the sputtering condition remains reactive after the elimination of just one Ti ribbon. The reason for the higher sputtering rate observed in this case is the result of the combination of two effects: i) the poisoning of the target is avoided due to the presence of Ti and ii) the higher deposition rate of Zr in the new area exposed after the removal of the Ti ribbon, which can be only noticed when the target is not poisoned.

Additionally, it is possible to see that the microstructure of the films remains very similar in these three cases, showing a dense microstructure with interrupted columns. In contrast, the

coating deposited in static mode has a more compact and fibrous structure with no trace of columnar development, which is probably a consequence of the lack of shadowing that takes place in this particular arrangement.

As it was described in Section 3.2, the sample deposited with 2 ribbons (TZ1.5-4.25) has a structure mainly composed by TiN, although a small peak of Zr-O-N can be still detected at ca. 56º. In the case of the film deposited with one ribbon (TZ1.5-4.25-1r), the sharp peaks in the diffractogram shift to lower angles, to positions located between the references of the TiN and ZrN phases. This indicates the formation of a solid solution of ZrN and TiN-based phases. This interpretation is in line with the behavior of the chemical composition, since when one Ti ribbon was removed, the Ti content decreased about 50% and it was replaced by Zr. It is worth mentioning that this film still presents the broad peak consistent with Zr-N-O phases (ca. 56º), similarly to the sample deposited with 2 ribbons. Finally, the coating deposited in static mode (TZ1.5-4.25-1rs) shows a similar structure than the film grown under rotation. However, this film does not include the broad peak related to Zr-O-N phases, and the peaks related to the solid solution are broader than in the previous case. Both facts suggest that the much higher deposition rate (factor 4) has led to the formation of a mixed phase of poorer crystallographic quality, instead the mixture of two phases. The removal of both Ti ribbons leads to the formation of a Zr oxynitride film with low order.

3.4. Analysis of phases and densities

The stoichiometry of some of the crystallographic phases formed by the elements Zr, Ti, O and N is included in Table 4, and plotted in Figure 10a [76]. The main characteristics of the selected phases are summarized in Tables 5-7 (metallic, nitrides, oxynitrides and oxides of Zr, Ti and Zr and Ti, respectively). A plot displaying the atomic density of these crystallographic

phases depending on their chemical composition is included as Supplementary Material. The atomic density is preferred over mass density, since the former just reflects the packaging of the different elements, while the latter incorporates also the atomic mass of the different elements.

For the following discussions, consider the orientation in Figure 10, with the non-metals (N and O) in the edge located at the bottom of the plot, and the metals (Ti and Zr) at the top edge. The binary compounds, located in the edges of the tetrahedron, are represented by red points in Figure 10a. The ternary and quaternary combinations are located in the four faces of the tetrahedron and in the volume, respectively, and they are represented with points of different colours. Each set is connected with lines of the corresponding colours to facilitate the visibility of the plot. It can be appreciated that there are several Zr-Ti metallic combinations in a range from 7 to 94% of Zr, which indicates an excellent miscibility of both metals. There are two types of system, cubic (space group #229) and hexagonal (#194), like the isolated elements. The atomic and mass densities of these alloys show opposite behaviours, from the values of pure Zr (4.2 and 4.3×10^{22} at/cm^3, 6.41 and 6.5 g/cm^3 for cubic and hexagonal, respectively) to pure Ti (5.7×10^{22} at/cm^3 and 4.50 g/cm^3). The number of nitride phases is lower than of oxides. The nitrides of Zr show higher oxidation states (o-Zr$_3$N$_4$, c-Zr$_3$N$_4$, and c-ZrN) than of Ti (c-TiN *Osbornite* and t-Ti$_2$N). The atomic densities of the nitrides (8.0-10.5$\times10^{22}$ at/cm^3) are clearly higher than the metals, while for the mass densities the difference between the nitrides and the correspondent metals is not so large. The mass density of the nitrides is higher, except in the case of o-Zr$_3$N$_4$ phase that shows a lower mass density than the pure Zr phases. The oxide phases are more numerous; Zr shows two Zr-rich oxide phases (r-Zr$_3$O and h-Zr$_3$O), whose densities are low, but higher than the density of Zr. Then, there are oxide phases isostructural to the cubic nitrides, but with slightly lower densities, c-ZrO and c-TiO (*Hongquiite*). There are two

tetragonal (*Rutile*, *Anatase*) and one orthorhombic (*Brookite*) phases of TiO_2, whose densities are in the range of 8.8-9.6×10^{22} at/cm^3 and 3.87-4.25 g/cm^3), and four ZrO_2 phases (monoclinic (*Baddeleyite*), cubic, tetragonal and orthorhombic), with densities of 8.5-10.7 at/cm^3 and 5.82-7.27 g/cm^3. Finally, between the Ti monoxide and the dioxide there is a family of O-deficient compounds, with generic formula Ti_xO_{2x-1}, with *x* in the range 2-10 (although higher values of *x* are reported [77–79]); these are the so-called Magnéli phases [80,81] (e.g. r-Ti_2O_3 or m-Ti_3O_5) and they show densities lower than the one of TiO. It is worth mentioning that there are phases with O/Zr>2, with densities lower (m-$Zr_{0.93}O_2$) and higher (c-$ZrO_{2.12}$) than the correspondent monoclinic and cubic ZrO_2 references, respectively.

The ternary compounds (nitrides and oxides of Zr with Ti and oxynitrides of Zr or Ti) are also included in Figure 10a. The nitrides of Zr and Ti lay in the line connecting ZrN and TiN, show the same structure (Fm-3m) and an intermediate density. This is similar to what happens with the oxides, excepting the Ti_2ZrO, which is located in a line connecting Ti and ZrO and show an intermediate density. The other oxides are in the line connecting TiO_2 and ZrO_2. They belong to a family of compounds labelled as *Srilankite*, all of them belonging to the same spatial group (#60), with densities in the range 9.0-9.4×10^{22} at/cm^3 and 4.85-5.21 g/cm^3. The Zr oxynitrides are all located in the line connecting Zr_3N_4 and ZrO_2; in contrast, the Ti oxynitrides are mostly located in an area limited by TiN, Ti_2N, TiO and TiO_2. One of them is located slightly over that region ($TiN_{0.31}O_{0.31}$) and three slightly below ($Ti_{0.68}N_{0.78}O_{0.36}$, $Ti_{2.85}NO_4$ and $TiN_{0.24}O_{1.88}$). In fact, all the references (except these three mentioned, plus the two Zr oxides with O/Zr ratio slightly larger than 2) are located above a region limited by the phases Zr_3N_4, ZrO_2, TiO_2 and TiN, which is represented in Figure 10 as a dashed area. This dashed area is a boundary where below it (closer to the O and N vertices), the concentration of N and O would be too high to form

stoichiometric solid compounds. Actually, the two oxynitrides of Zr and Ti found are located on top ($Ti_{0.5}Zr_{0.5}N_{0.615}O_{0.96}$) or slightly over ($TiZrN_{1.9}O_{1.06}$) that boundary.

The location of the films presented in this paper in the same quaternary plot is shown in Figure 10b. The crystallographic binary references have been left in the plot for an easier correspondence with Figure 10a. The Zr-O-N films are located in the back face of the tetrahedron. Those films with stronger metallic character (Z2.0-2.5 and Z2.0-3.75) are very close to the Zr-N edge, and they show densities (4.4 and 5.1×10^{22} at/cm^3) which are between that of Zr (4.2-4.3 $\times10^{22}$ at/cm^3) and ZrN (8.3×10^{22} at/cm^3). When the concentration of non-metal elements increases, the position of the films approaches the Zr_3N_4-ZrO_2 line. The following couple of films (Z2.0-4.0 and Z2.0-4.25) show much higher densities than the previous ones (7.1 and 7.5×10^{22} at/cm^3), which are in the range of near references, such as c-Zr_2ON_2 and ZrN (7.7 and 8.3×10^{22} at/cm^3, respectively), which are the phases detected by XRD in these films (cf. Figure 4b). Finally, for the final four films identified as 'poisoned' the density decreases again to values of 6.6-6.7$\times10^{22}$ at/cm^3, which would be a consequence of the additional oxygen in the structure reducing its atomic density (cf. densities of ZrN vs. ZrO). The exception is the final film (Z1.5-4.25), which shows an unexpectedly high density of 8.1×10^{22} at/cm^3, which is close to the value of the $Zr_7O_8N_4$ (8.2×10^{22} at/cm^3). Nevertheless, the location of this film in this diagram shows that it is below the 'boundary line' connecting Zr_3N_4 and ZrO_2. Therefore, in this case, there would be an excess of N and O atoms interstitial in the lattice, explaining the high value of density observed.

Tables 2 and 3 include a chemical ratio defined as:

$$MN = \frac{Zr+Ti-O/2}{N}$$

That expression calculates the metal-to-nitrogen ratio, excluding the metal bonded to oxygen

under the assumption that it is in form of metal dioxides. For Zr-O-N films (Table 2), the expected values would be in the range (0.75-1), which correspond to Zr_3N_4 and ZrN, respectively. Most of the films are in that range or close to it, which indicates that, chemically speaking, the films can be interpreted as a combination of oxide and nitride. Films Z2.0-2.5 and Z2.0-3.75 show large values of this parameter (4.71 and 2.20), indicating an excess of Zr and their metallic character. In contrast, film Z1.5-4.25 shows a value of 0.61, which is below the minimum and supports the presence of interstitial atoms in this film.

Films including Ti are represented with three different series in Figure 10b and c (zoomed view in a different angle). Solid and hollow blue points represent the films deposited at 1.5 A and 2.0 A, respectively, while the films deposited with 1 Ti ribbon are represented with pink points. Both films closer to the Zr-N-O face are those deposited at the lowest N_2+O_2 flow at both target currents (films TZ2.0-4.25 and TZ1.5-2.5). In both series, the increase of N_2+O_2 flow lead to a similar type of displacement, in direction to the O corner towards the 'boundary surface'. Thus, for the films deposited at 2.0 A, the O/(Zr+Ti) ratio increases from 0.29 to 0.70, while the MN ratio decreases from 1.08 to 0.74 (i.e. around the lower limit). The three films deposited at 1.5 A at lowest N_2+O_2 flow show a similar trend, with O/(Zr+Ti) increasing from 0.21 to 0.30 to 0.42, and the MN ratio decreasing from 1.15 to 1.07 to 0.87. The three films deposited at 1.5 A at the highest flows of N_2+O_2 are located very close in the quaternary diagram as a result of their similar chemical composition (cf. Figure 3c), and show similar values of both ratios. Both films deposited with 1 Ti ribbon are located near the boundary, as film TZ1.5-4.25, but farther from the Ti vertex (lower Ti concentration). The film deposited in static mode moves to the left (farther from the O vertex) due to the lower O concentration.

For Ti:Zr-O-N films, it is very difficult to interpret the variations of density as in case of the

Zr-O-N films; one of the reasons is that there is a complex variation of phases present in the films, as illustrated in Figures 4 and 8 (co-existence and formation of mixed phases). Nevertheless, some observations can be made; in agreement with what was exposed for the crystallographic phases, the density of the films including Ti is similar or higher than the films without Ti deposited under the same synthesis conditions. In fact, both films with highest Ti concentration (TZ1.5-3.75 and TZ1.5-4.25) show the highest values of density of all films (7.9 and 8.2×10^{22} at/cm^3), excepting Z1.5-4.25 whose special characteristics were explained before. The reduction of the number of Ti ribbons in the racetrack (in films from Figures 7, 8 and 9) causes a decrease of density from 7.9 to 7.5 to 6.8×10^{22} at/cm^3. Overall, the values of density of the Ti:Zr-O-N films are lower than the Ti-O-N references and closer to the Zr-O-N references of similar chemical characteristics (cf. Tables 6 and 7 and density plots in Supplementary material). Those values are in agreement with the co-existence of Zr-O-N and Ti-O-N phases and the formation of mixed Ti-Zr-N-O phases.

3.5. Colour and electrical properties of the films

The color coordinates and electrical properties of the films are summarized in Tables 2 and 3. The first point to be noticed is that all transparent films show an 'amorphous' XRD structure, i.e. that in agreement to the shapes of the patterns enclosed in Figure 4a (deposited without Ti at 1.5 A). In fact, the two other films with that amorphous structure (Z2.0-4.75 and TZ2.0-4.75) are in the limit of opacity, while all the films with a different XRD structure show opacity and color. This observation reveals that a well-formed crystallographic structure seems to be a critical requirement for films with intrinsic color. The chromaticity coordinates (a*, b*) of the non-transparent films are depicted in Figure 11a, on a 'color wheel' that represents the different colors for each (a*, b*) couple. All the films lay in the same area, regardless the presence of Ti.

This indicates that the introduction of Ti does not cause a dramatic modification of the colors of the films. Figure 11b is a zoomed view of Figure 11a in the area where the samples are located. Since the Z1.5 films are all transparent, we can identify only four series of samples, which are summarized in the top of Figure 11b. The internal variable in these series is the flow of N_2+O_2, except for the series of films deposited with 1 Ti ribbon, in which the variable is the presence of substrate rotation. That internal variable is included next to each point, and together with its color (green, blue, orange or red), allows to identify univocally the synthesis condition of each film. The dashed black arrows indicate the connection between series.

The first observation is that films can be divided into two groups; the first one, highlighted in a grey area in Figure 11b, corresponds to films with similar color coordinates ($50.4 < L^* < 52.5$, $0.8 < a^* < 5.5$ and $-3.9 < b^* < 1$), while the other films are distributed in a wider area. The films of the second group share two characteristics: i) an oxygen-to-metal ratio $O/(Zr+Ti)<0.3$, and ii) they show well-defined peaks of Zr-O-N phases, including films TZ1.5-2.5 and TZ1.5-3.75, with the peak at ca. 34°. Both facts are probably correlated, since the Zr-O-N phases tend to lose order at higher O contents, while Ti-O-N phases are still relatively well formed (cf. Figure 4c). The formation of mixtures of Zr-O-N and Ti-O-N phases (Figure 8) is not enough to escape the region of the films with similar color coordinates.

In general, it can be appreciated that the increase of N_2+O_2 flow causes a similar effect in the three series, which corresponds to what described in our previous work with Zr-O-N films [16]. Thus, the Z2.0 films (green color in Figure 11b) show a grey color ($a^*\sim1$, $b^*\sim7.5$) when deposited at low N_2+O_2 flows (2.50 and 3.75 sccm), in agreement with their metallic character. Increasing the flow, the color changes to golden (4.00 sccm, Zr nitride), reddish (4.25 sccm, Zr nitride and oxynitride) and slightly bluish in the limit of opacity (4.75 sccm, disordered Zr

oxynitride). Both TZ2.0 films (blue color in Figure 11b) show similar characteristics to films of the Zr-O-N series, as described in Section 3.2, and the color coordinates follow that explanation very well. Both films are located in the path of the Zr-O-N films (green line in Figure 11b); in the one hand, the film deposited at 4.25 sccm is situated between the Zr-N-O films deposited at 3.75 and 4.00 sccm, but closer to this latest one. In the other hand, the film deposited at 4.75 sccm is located in the region of low values of a* and b*, near the correspondent film prepared without Ti.

The TZ.15 films (orange color in Figure 11b) show a similar overall trend. The films prepared at 2.50 sccm show grey color, similarly to both 'metallic' Zr-O-N films. This is in agreement with the broad Zr (oxy)nitride peaks detected for film TZ2.0-4.25 (cf. the peak at ca. 34º in Figure 4d). The film deposited at 3.75 sccm shows a displacement in the same direction as the Z2.0 films deposited at 4.00 and 4.25 sccm, but of smaller magnitude. This is the only film which is composed by a mixture of well-formed Zr-O-N and Ti-O-N phases, which suggests that the presence of Ti-O-N phases reduces the palette of colors achievable, in line with what described previously. The films of this series prepared with higher N_2+O_2 flows (4.00, 4.25 and 4.75 sccm) show dominant Ti-O-N phases, and they are located in the region of films with similar color coordinates. In that region are also located the films deposited with 1 Ti ribbon, which are formed by Zr-Ti-O-N phases.

Figure 12 shows the color coordinates and electrical properties of the different films depending on the oxygen-to-metal ratio O/(Zr+Ti) measured by RBS. A similar plot including the same chemical ratio measured by EDX has been included as Supplementary Material, and it shows equivalent trends although the values of the O/(Zr+Ti) ratio differ. It can be seen that all films are very nicely ordered using that parameter, regardless the synthesis condition (flow,

current, number of Ti ribbons, rotation). To a certain extent, this is quite surprising, since the N concentration is not considered in that parameter. Nevertheless, it is worth mentioning that films without N (i.e. Zr-O and Zr-Ti-O) would show very different properties, so its presence is mandatory to obtain the properties of the films described in this paper. The reason for that parameter to work so smoothly may be related to the fact that the N concentration is similar for most of the films.

The color coordinates of the different films are depicted in Figure 12a. The films with O/(Zr+Ti)>0.3 show constant values of these parameters, and correspond to the family of films with similar color indicated before (grey area in Figure 11b). For the other films, the lightness coordinate L* show a smooth reduction from ca. 70 to 50, while a* and b* show maxima (more intense for b*) before reaching the region of steady values. That behavior corresponds to the trajectories depicted in Figure 11b. Interestingly, the electrical resistivity of the films also show a common trend (red points Figure 12b). The values are low for films with low O/(Zr+Ti), but the resistivity shows an exponential growth (notice the logarithmic scale) when O/(Zr+Ti) varies from ~0.2 to 0.4. This can be easily interpreted as a progressive electrical isolating character of the films as the O concentration increases (more 'ceramic'). Those samples whose resistivity was too high for our measurement approach were classified as insulators, and subjected to an additional evaluation of their dielectrical behavior, by means of the dielectric loss tangent (tan□). That parameter represents the loss of dielectric capability of the material (conductive losses) respect to its dielectric capability. The decrease of tan□ with increasing frequency, observed in all samples (cf. Figure 2, bottom), is attributed to a low charge dynamics: the hopping frequency of charge carriers, including interfacial contributions, cannot follow the changes of the externally applied electric field for larger frequencies [82]. The values of tan□ at

1 kHz are represented on the right y axis in Figure 11b (blue points). It is worth mentioning that there are three of these films do not appear in Figure 11a, since these films are transparent. It is observed that the dielectric loss decreases with the O/Zr ratio, indicating that the conductive loss of the films is reduced when the O content increases, as it can be expected. It is interesting to say that the Ti containing film considered as an 'insulator' shows a larger value of tanδ than the films without Ti for similar O/(Zr+Ti) ratios, in contrast to the good agreement observed for the resistivity values. That would indicate that the presence of Ti favors the conductivity of the film. In fact, films including Ti remain conductive up to O/(Zr+Ti) 0.43, while the first film without Ti with isolating character appears at O/Zr~0.36; this observation supports the enhancement of conductivity when Ti is present in the films.

Considering the correlation of color and resistivity with the same chemical ratio, we attempted at plotting the color coordinates against the electrical resistivity of the films (Figure 13). In general, the agreement is reasonably good, indicating that films with certain resistivity will show a certain color. However, two films with resistivity around 1.6 mΩ·cm show significantly different values of L* and b*. These films are Z2.0-4.0 and TZ1.5-3.75, which correspond to a reasonably well-formed Zr-O-N, and a film with co-existing Zr-O-N and Ti-O-N phases, respectively (cf. Figure 4b and c). It can be noticed that, although the electrical conductivity is similar for both, the film including Ti has lower values of the color coordinates, e.g. smaller palette of colors achievable.

4. Conclusions

In this work Zr-O-N films including Ti have been deposited with a simple approach that consisted in the location of Ti ribbons on top of the Zr target. The use of Ti seems to retard the passivation of the target, and a so-called Poisoning Parameter has been defined to illustrate that

effect. Nevertheless, the incorporation of Ti is lower at higher target currents, since the relative sputtered area occupied by the Ti ribbons is smaller. Therefore, under those situations, the Ti incorporation can be considered as a small perturbation from the Zr-O-N system. In contrast, at low target currents, the introduction of Ti is characterized by the formation of Ti-O-N phases and also solid solutions including Zr, in contrast to disordered Zr-O-N films deposited in similar conditions. In general, the Ti:Zr-O-N films can be interpreted as mixtures of ZrO_2, TiO_2, Zr_3N_4 and TiN phases, in line with what it is described for reference crystallographic phases. The color and electrical properties of the films could be interpreted in terms of their phase and chemical composition. Those presenting a disordered structure showed a certain degree of transparency, while the others could be divided into two groups. Films with well-formed Zr-O-N phases showed a larger variation of color coordinates, while the others were located in a much smaller region. In that regard, the presence of Ti-O-N phases did not contribute to widen the palette of colors available for Zr-O-N. The electrical resistivity of all the films increased with the oxygen-to-metal ratio, which also correlated with the color coordinates. The presence of Ti in the film promoted the conductivity of the films.

Acknowledgements

5. References

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Table 1. Sample codes of the films described in this paper, depending on the target employed (Zr or Ti:Zr), current (1.5 or 2 A) and flow of mixture of reactive gases (2.50, 3.75, 4.0, 4.25 and 4.75 sccm). In addition, two of the films have been prepared with 1 Ti ribbon with and without rotation of the sample holder (TZ1.5-4.25-1r and TZ1.5-4.25-1rs, respectively).

Target		Flow of N_2+O_2 (sccm)				
Material	Current (A)	2.50	3.75	4.0	4.25	4.75
Zr	1.5		Z1.5-3.75	Z1.5-4.0	Z1.5-4.25	
	2.0	Z2.0-2.5	Z2.0-3.75	Z2.0-4.0	Z2.0-4.25	Z2.0-4.75
Ti:Zr	1.5	TZ1.5-2.5	TZ1.5-3.75	TZ1.5-4.0	TZ1.5-4.25 TZ1.5-4.25-1r TZ1.5-4.25-1rs	TZ1.5-4.75
	2.0				TZ2.0-4.25	TZ2.0-4.75

Table 2. Characteristics of the Zr-O-N films. Color coordinates in *italics* indicate a film in the limit of opacity.

Sample	Deposition rate (nm/h)	Chemical comp. (at. %)			Chemical ratios			Density		Color coordinates			Resistivity (mΩ·cm)	tan□ at 1 kHz
		Zr	O	N	$\frac{O+N}{Zr}$	$\frac{O}{Zr}$	$\frac{Zr+Ti-O/2}{N}$	$\times10^{22}$ at/cm^3	g/cm^3	L*	a*	b*		
Z2.0-2.5	1390	82	1	17	0.23	0.02	4.71	4.4	5.41	71.8	0.8	7.1	0.267	-
Z2.0-3.75	1180	68	1	31	0.47	0.02	2.20	5.1	6.27	69.9	1.2	8.2	0.275	-
Z2.0-4.0	813	45	11	44	1.19	0.23	0.92	7.1	5.82	62.9	4.4	28.?	1.63	-
Z2.0-4.25	686	43	13	44	1.31	0.29	0.84	7.5	5.92	56.5	?.1	21.4	2.78	-
Z2.0-4.75	625	47	17	36	1.13	0.36	1.07	6.7	5.60	*5?.0*	*?.?*	*-3.9*	overflow	1.15
Z1.5-3.75	418	42	24	34	1.39	0.57	0.88	6.6	5.12	Transparent			overflow	0.66
Z1.5-4.0	396	40	26	34	1.53	0.67	0.77	6.7	4.?8	Transparent			overflow	0.13
Z1.5-4.25	373	36	30	34	1.80	0.84	0.61	8.?	5.71	Transparent			overflow	0.10

Table 3. Characteristics of Ti:Zr-O-N films. Color coordinates in *italics* indicate a film in the limit of opacity. Films TZ2.0-4.25 and

TZ1.5-4.25-1rs were deposited during 30 minutes instead 60.

Sample	Deposition rate (nm/h)	Chemical comp. (at. %)				Chemical ratios				Density		Color coordinates			Resistivity (mΩ·cm)	tan□ at 1 kHz
		Zr	Ti	O	N	$\frac{O+N}{Zr+Ti}$	$\frac{O}{Zr+Ti}$	$\frac{Zr}{Zr+Ti}$	$\frac{Zr+Ti-O/2}{N}$	$\times10^{22}$ at/cm^3	g/cm^3	L*	a*	b*		
TZ2.0-4.25	965	37	11	14	38	1.08	0.29	0.78	1.08	7.2	5.58	63.6	3.4	22.3	0.732	-
TZ2.0-4.75	597	29	10	27	34	1.58	0.70	0.75	0.74	7.5	5.00	*51.0*	*3.9*	*1.3*	overflow	3.63
TZ1.5-2.5	797	35	15	11	39	0.99	0.21	0.69	1.15	6.7	5.14	71.8	1.1	9.8	0.263	-
TZ1.5-3.75	665	27	21	14	38	1.09	0.30	0.56	1.07	8.2	5.72	55.8	5.7	15.5	1.57	-
TZ1.5-4.0	460	26	17	18	39	1.32	0.42	0.60	0.87	6.5	4.31	50.4	3.3	-2.0	78.6	-
TZ1.5-4.25	468	22	21	19	38	1.31	0.43	0.50	0.89	7.9	5.04	50.7	2.8	-3.0	28.2	-
TZ1.5-4.75	581	25	19	16	40	1.29	0.37	0.57	0.88	7.1	4.72	51.2	3.9	-1.1	17.4	-

| TZ1.5-4.25-1r | 546 | 32 | 12 | 17 | 39 | 1.29 | 0.40 | 0.73 | 0.90 | 7.5 | 5.34 | 51.1 | 4.7 | 1.0 | 48.8 | - |
| TZ1.5-4.25-1rs | 2140 | 31 | 12 | 14 | 43 | 1.35 | 0.33 | 0.73 | 0.82 | 6.8 | 4.73 | 52.5 | 5.4 | -1.0 | 5.54 | - |

Table 4. Stoichiometries of some crystallographic phases formed by Zr, Ti, O and N. These combinations are represented in Figure 10a, and detailed in Tables 5-7.

Non-metallic elements	Metallic elements		
	Zr	Ti	Zr, Ti
-	Zr	Ti	Zr_xTi_{1-x}, $x \in [0.07, 0.94]$
N	ZrN, Zr_3N_4	Ti_2N, TiN	$ZrTiN_2$ $Zr_{0.42}Ti_{0.58}N_2$
O	Zr_3O, ZrO, ZrO_2	TiO, TiO_2 Ti_xO_{2x-1}, $x \in [4, 10]$	$ZrTi_2O$ $Zr_xTi_{1-x}O_2$, $x \in [0.33, 0.575]$
O, N	$ZrO_{2-x}N_{2x/3}$ $x=0.43, 0.64, 0.86, 1.5$	TiO_xN_y $x \in [0.05, 1.88]$ $y \in [0.21, 0.74]$	$ZrTiO_{1.06}N_{1.9}$ $ZrTiO_{1.92}N_{1.23}$

Table 5. Characteristics of some crystallographic phases formed by Zr, O and N.

Phase	$\dfrac{O+N}{Zr}$	$\dfrac{O}{O+N}$ (%)	M/n_{Zr} (g/mol)	Density $\times 10^{22}$ at/cm^3	g/cm^3	Crystal system*	Space group		PDF Reference
Zr	0	-	91.2	4.2	6.41	c	Im-3m	229	1-89-4916
Zr	0	-	91.2	4.3	6.51	h	P6$_3$/mmc	194	0-5-0665
ZrN	1	0	105.2	8.3	7.29	c	Fm-3m	225	0-35-0753
Zr$_3$N$_4$	1.33	0	109.9	8.1	6.34	o	Pnma	62	1-87-0842
Zr$_3$N$_4$	1.33	0	109.9	9.1	7.15	c	I-43d	220	1-72-8064
Zr$_2$ON$_2$	1.5	33	113.2	7.7	5.78	c	Ia-3	206	0-50-1170
Zr$_7$O$_8$N$_4$	1.71	67	117.5	8.2	5.88	r	R-3	148	0-50-1172
Zr$_7$O$_{9.5}$N$_3$	1.79	76	118.9	-	-	r	P-3 (?)	147 (?)	[83,84]
Zr$_7$O$_{11}$N$_2$	1.86	85	120.4	-	-	r	R-3	148	0-48-1637
Zr$_3$O	0.33	100	96.6	5.7	6.90	r	P32	155	0-22-1025
Zr$_3$O	0.33	100	96.6	5.6	6.79	h	P6$_3$22	182	1-89-8002
ZrO	1	100	107.2	8.1	7.22	c	Fm-3m	225	0-20-0684
ZrO$_2$	2	100	123.2	8.5	5.82	m	P2$_1$/c	14	0-37-1484
ZrO$_2$	2	100	123.2	8.9	6.07	c	Fm-3m	225	0-49-1642
ZrO$_{1.98}$	1.98	100	123.2	8.6	5.88	t	P4$_2$/nmc	137	1-81-1548
ZrO$_2$	2	100	123.2	10.7	7.27	o	Pnma	62	1-83-0810
Zr$_{0.93}$O$_2$	2.15	100	125.6	8.2	5.40	m	P2$_1$/c	14	0-81-1381
ZrO$_{2.12}$	2.12	100	125.1	9.2	6.16	c	Fm-3m	225	0-81-1550

*c: cubic, t: tetragonal, h: hexagonal, r: rhombohedral, o: orthorhombic, m: monoclinic.

Table 6. Characteristics of some crystallographic phases formed by Ti, O and N.

Phase	$\dfrac{O+N}{Ti}$	$\dfrac{O}{O+N}$ (%)	M/n_{Ti} (g/mol)	Density $\times 10^{22}$ at/cm^3	g/cm^3	Crystal system*	Space group		PDF Reference
Ti	0	-	47.9	5.7	4.50	h	P6$_3$/mmc	194	0-44-1294
Ti$_2$N	0.5	0	54.9	8.0	4.83	t	I4$_1$/amd	141	1-73-0959
Ti$_2$N	0.5	0	54.9	8.1	4.91	t	P4$_2$/mnm	136	1-76-0198
TiN	1	0	61.9	10.5	5.38	c	Fm-3m	225	0-38-1420
TiN$_{0.6}$O$_{0.4}$	1	40	62.7	10.0	5.22	c	Fm-3m	225	0-49-1325
TiN$_{0.74}$O$_{0.34}$	1.08	31	63.7	-	-	m	-	-	0-44-0951
Ti$_{2.85}$NO$_4$	1.75	80	75.2	8.7	3.93	o	Cmcm	63	1-76-9463

Phase										
TiO	1	100	63.9	10.1	5.36	c	Fm-3m	225	1-86-2352
Ti_2O_3	1.5	100	71.9	9.6	4.59	r	R-3c	167	0-10-0063
Ti_3O_5	1.67	100	74.5	9.4	4.35	m	C2/c	15	0-40-0806
TiO_2	2	100	79.9	9.6	4.25	t	$P4_2/mnm$	136	0-21-1276
TiO_2	2	100	79.9	9.3	4.12	o	Pbca	61	0-29-1360
TiO_2	2	100	79.9	8.8	3.89	t	$I4_1/amd$	141	0-21-1272
TiO_2	2	100	79.9	8.8	3.87	o	Pnma	62	0-49-1433

*c: cubic, t: tetragonal, h: hexagonal, r: rhombohedral, o: orthorhombic, m: monoclinic.

Table 7. Characteristics of some crystallographic phases formed by Zr, Ti, O and N.

Phase	$\frac{O+N}{Zr+Ti}$	$\frac{O}{O+N}$ (%)	$\frac{Zr}{Zr+Ti}$ (%)	M/n_{Zr+Ti} (g/mol)	Density $\times 10^{22}$ at/cm^3	g/cm^3	Crystal system*	Space group		PDF Reference
$Ti_{0.06}Zr_{0.94}$	0	-	94	88.6	4.6	6.79	h	$P6_3/mmc$	194	1-82-3000
$Ti_{0.1}Zr_{0.9}$	0	-	90	86.9	4.3	6.21	c	Im-3m	229	1-82-3002
$Ti_{0.3}Zr_{0.7}$	0	-	70	78.2	4.6	6.01	h	$P6_3/mmc$	194	1-72-3354
TiZr	0	-	50	69.5	4.9	5.68	c	Im-3m	229	1-72-3352
TiZr	0	-	50	69.5	4.9	5.63	h	$P6_3/mmc$	194	3-65-9625
$Ti_{0.67}Zr_{0.33}$	0	-	33	62.2	5.1	5.27	h	$P6_3/mmc$	194	1-72-3353
$Ti_{0.89}Zr_{0.11}$	0	-	11	52.6	5.3	4.64	c	Im-3m	229	1-82-3001
$Ti_{1.83}Zr_{0.17}$	0	-		51.6	5.5	4.73	h	$P6_3/mmc$	194	1-77-3485
$Ti_{0.93}Zr_{0.07}$	0	-	7	50.9	5.4	4.58	h	$P6_3/mmc$	194	1-82-2999
$TiZrN_2$	1	0	50	83.6	9.2	6.37	c	Fm-3m	225	1-77-3008
Ti_2ZrO	0.33	100	33	67.7	6.6	5.60	o	Cmmm	65	1-71-0840
Ti_2ZrO	0.33	100	33	67.7	6.6	5.58	h	P6/mmm	191	1-72-1881
Ti_2ZrO_6	2	100	33	94.3	9.3	4.85	o	Pbcn	60	0-46-1265
$Ti_{0.65}Zr_{0.35}O_2$	2	100	35	95.0	9.2	4.86	o	Pbcn	60	1-74-9435
$Ti_{0.6}Zr_{0.4}O2$	2	100	40	97.2	9.2	4.94	o	Pbcn	60	1-74-9434
$Ti_7Zr_5O_{24}$	2	100	42	97.9	9.4	5.07	o	Pbcn	60	0-34-0209
$Ti_{0.548}Zr_{0.452}O_2$	2	100	45	99.5	9.1	5.00	o	Pbcn	60	1-74-9433
$TiZrO_4$	2	100	50	101.5	9.0	5.08	o	Pbcn	60	0-34-0415
$Ti_{0.45}Zr_{0.55}O_2$	2	100	55	103.7	9.0	5.16	o	Pbcn	60	1-74-9431
$Ti_{0.425}Zr_{0.575}O_2$	2	100	58	104.8	9.0	5.21	o	Pbcn	60	1-74-9430

*c: cubic, t: tetragonal, h: hexagonal, r: rhombohedral, o: orthorhombic, m: monoclinic.

Figure captions

Figure 1. Schematic representation of the location of Ti ribbons on top of the racetrack of the Zr target for introduction of Ti in the films: a) Lateral view of the target and substrate holder. b) Detail of the Ti ribbon attachment. 1 Titanium ribbons, 2 Zirconium target, 3 Pieces of glass, 4 Substrate holder, 5 Steel pieces.

Figure 2. Geometries employed for the measurement of electrical properties. Top: measurements of electrical resistivity, with the V-I curves of two representative films showing the typical Ohmic behavior (dashed lines are linear fits). Bottom: measurements of dielectric properties, with some curves of dielectric loss tangent vs. frequency. 1: electrical probes. 2: film. 3. substrate (glass and steel, respectively).

Figure 3. Chemical composition and deposition rate of films prepared without Ti (a, b) and with Ti (c, d) with target currents of 1.5 A (a, c) and 2.0 A (b, d), and different flows of reactive mixture.

Figure 4. Diffractograms of the films prepared without Ti (a, b) and with Ti (c, d) with target currents of 1.5 A (a, c) and 2.0 A (b, d). The flows of reactive mixture (in sccm) are included in each diffractogram. For clarity, the Miller indexes of the Zr-O-N phases are indicated only in the left column (the indexes are the same for ZrO and ZrN phases, since both are isostructural), while the indexes of the TiN phase are indicated only in the right column.

Figure 5. Cross section SEM micrographs of films prepared without and with Ti with target currents of 1.5 A and 2.0 A and different flows of reactive gas. The scale bars represent 500 nm.

Figure 6. Variation of the Poisoning Parameter (PP) for Zr-O-N and Ti:Zr-O-N films prepared at different values of target current and flow of N_2+O_2. Since all the Zr-O-N films can be interpreted as a combined set, series prepared at 2.0 and 1.5 A appear connected with a dashed line.

Figure 7. Influence of the number of Ti ribbons and substrate rotation on the chemical composition and deposition rates of films prepared at 1.5 A and 4.25 sccm of N_2+O_2.

Figure 8. Influence of the number of Ti ribbons and substrate rotation on the XRD patterns of films prepared at 1.5 A and 4.25 sccm of N_2+O_2. The Miller indexes of the crystalline phases are indicated next to the references; only one label is indicated for ZrO and ZrN phases, since both are isostructural.

Figure 9. Influence of the number of Ti ribbons and substrate rotation on the growth of films prepared at 1.5 A and 4.25 sccm of N_2+O_2. The scale bars represent 500 nm.

Figure 10. Quaternary Zr-Ti-O-N compositional diagram of selected crystallographic phases from literature (a), and films included in this work (b). The surface connecting the Zr_3N_4-ZrO_2-TiO_2-TiN points is indicated with dashed lines. A zoomed view of the area around the location of the Ti:Zr-O-N films is shown in (c). This view is taken laterally from the Zr-Ti-N face.

Figure 11. Chromaticity coordinates a* and b* of the different series of films. a) Color wheel indicating the general location of the different samples. b) Detailed view of the central region. The colored continuous lines correspond to the different series of films, while the dashed black lines indicate the variations between series. The grey area highlights a region where all the films show similar color coordinates (see text for details).

Figure 12. Color and electrical properties of the films depending on the oxygen-metal ratio. a) Color coordinates (L*, a*, b*). b) Resistivity and dielectric loss tangent.

Figure 13. Correlation between color and electrical resistivity of the different films.

Declaration of competing interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Credit Author Statement

C. I. da Silva Oliveira: Formal analysis, Investigation, Writing - Original Draft, Visualization; **D. Martínez-Martínez**: Conceptualization, Methodology, Formal analysis, Resources, Writing - Review & Editing, Visualization, Project administration, Funding acquisition **L. Cunha**: Resources, Writing - Review & Editing, Supervision, Project administration, Funding acquisition; **S. Lanceros-Mendez**: Conceptualization, Resources ; **P. Martins**: Investigation, Resources; **E. Alves**: Investigation, Resources; **N. P. Barradas**: Investigation, Resources; **M. Apreutesei**: Investigation, Resources.

Highlights

- Zr-O-N films with Ti were sputtered from a Zr target with Ti ribbons in the racetrack.
- The effect of target current and reactive flow was explored versus films without Ti.
- The Ti ribbons retards poisoning of the target, accounted with an 'ad-hoc' parameter.
- The coexistence of Zr-O-N and Ti-O-N phases is observed, and also mixed phases.
- Color and electrical properties depend on the oxygen-to-metal ratio, N seems passive.