Evaluation of thermal properties of thin films by IR radiometry using a comprehensive set of Zr-O-N thin films

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Abstract

Modulated Infrared Radiometry is a photothermal technique which allows thermal characterization of coatings. Thermal properties are determined by applying the "Extremum Method". Zr-O-N films were deposited by sputtering to evaluate their thermal properties and the sensitivity of the method and its suitability for different film+substrate systems. Three factors were varied: i) composition/bonding: metallic Zr, crystalline metallic-type Zr-O-N and disordered ceramic Zr-O-N. The films were deposited in the metallic, reactive and poisoned regimes of the hysteresis curve; ii) each film was deposited simultaneously on three different substrates: high-speed steel, glass and silicon; iii) in each deposition batch, films with four different thicknesses were grown. Each film was deposited in the same batch with different thicknesses on top of different substrates. All of the parameters for which the model is sensitive to are explored in this matrix of 36 different samples. The thermal parameters of the films were calculated and the trends and values were examined. The trends were explained in terms of the microstructural/chemical characteristics of the films, and the influence of each substrate, depending on the film thickness. The obtained values agree with those found in literature, reflecting the nature of the films.

Keywords: Zirconium oxynitride; Modulated Infrared Radiometry; Thermal conductivity; Volumetric heat capacity; Effusivity; Diffusivity

1. Introduction

Modulated infrared radiometry is a photothermal technique based on the creation of small temperature oscillations, usually called "thermal waves", by means of modulated heating of a

material, and on the detection of the thermal response using an IR detector connected to a lock-in amplifier [1]. Once the penetration depth of the incident radiation can be controlled just by controlling the modulation frequency of the incident radiation, the technique is widely used for the thermal characterization of thin films and coatings [2]. This technique is also appropriate for remote detection in deposition chambers and industrial applications [3,4]. The amplitude and phase lag of the recorded thermal wave contains all the information needed to determine the relevant thermal properties of a two layer system. Using an inverse solution of the two-layer thermal wave problem, direct relations can be established between the relative extrema of the inverse calibrated thermal wave phase lag signals, measured as a function of the heating modulation frequency, and fundamental thermal parameters of thin films and coatings, namely the ratio of the thermal effusivities coating-to-substrate, the coating's thermal diffusion time, and the coating thickness [4].

The goal of this work is twofold. First, to obtain the thermal characteristics of the three different types of Zr-O-N films, deposited in the metallic, reactive and poisoned regimes of the hysteresis curve. Second, to test the sensitivity of the technique to all the parameters included in the two-layer model, by taking advantage of the systematic approach employed during the film deposition which led to three different Zr-O-N films deposited during four deposition times (from 1 to 4 hours) on top of three different substrates (high speed steel, silicon and glass).

2. Experimental details

2.1. Thin film deposition and characterization

Zr-O-N thin films were deposited onto (111) silicon pieces (1.5 cm $\times$ 1.5 cm), glass (2 cm $\times$ 2 cm) and mirror-polished high-speed steel (HSS) cylindrical substrates ($\varnothing$=3 cm $\times$ 0.5cm) by reactive direct current magnetron sputtering in a laboratorial size deposition equipment. The substrates were first cleaned with ethanol and etched in a Zepto Plasma System (Diner) equipped with a 40 kHz / 100 W generator. During the etching process, the power used was 100 W and the Ar pressure was approximately 80 Pa. For the depositions, the substrates were clamped in a rotating holder (5 rpm) placed at 75 mm from the magnetron head. The base pressure was always below 2.6×10^{-3} Pa. The depositions were performed by sputtering of a Zr target (99.6 % at., 10×20 cm^2) using Ar as working gas and N$_2$ and O$_2$ as reactive gases. During the deposition, the discharge parameters (target potential, applied current and working pressure) were monitored 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.

In previous papers the influence of different deposition parameters (e.g. flow of the reactive mixture, bias, doping with Ti…) in the characteristics and optical properties of Zr-O-N films has been investigated[5,6]. Three different sets of synthesis conditions (Metallic, Reactive and Poisoned, henceforth referred as M, R and P films, respectively) were distinguished, which lead to 3 clear types of films: metallic Zr (metallic grey color, films M), crystalline Zr-O-N (golden, films R) and disordered Zr-O-N (transparent to visible radiation, films P). These conditions were chosen to deposit three different sets of films using different N_2 and O_2 flows (see Table 1), while maintaining the remaining conditions constant (Ar flow 18 sccm, Zr target current 2 A).

Additionally, for each of the three sets of films four different deposition times were used. In this manner 36 different samples were deposited (3 different film types, 4 different thicknesses and 3 different substrates). To optimize the depositions and keep the conditions of the films of the same type (M, R or P) exactly the same, the samples with different deposition times were deposited in the same batch. To do that, the substrates were clamped on four faces of the holder, and three of them were covered with a metallic shield at the beginning of the deposition (see Figure 1a). The deposition of each type of film was carried on during four hours, and one of the shields was removed after each hour in order to expose a new set of substrates (Si, glass and steel) to the plasma. At the end, four different thicknesses were obtained for each deposition batch, as summarized in the scheme of Figure 1b. The thickest films were growing for 4 hours, while the thinnest ones grew only for the last hour of the deposition process, which constitutes the top part of the thicker films (Figure 1b).

The chemical composition of the films was determined by Rutherford backscattering spectrometry (RBS) on the samples deposited during 2 h, using CTN/IST Van der Graaff accelerator in a small chamber were tree detectors were installed: standard at 140º, and two pin-diode detectors located symmetrically to each other both at 165º. 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 v9.6i [7], double scattering and Pileup were calculated using the algorithms given elsewhere[8,9]. The density and thickness of the films have been also calculated. The chemical composition was also investigated through Energy-dispersive X-ray spectroscopy (EDX) for the samples deposited during 1h and 4h in an EDAX -Pegasus X4M (EDS/EBSD) equipment operating at 10 kV.

1   The morphology of the films was characterized by scanning electron microscopy (SEM)

2 in a FEI - Nova 200 NanoSEM (FEG/ESEM) equipment operating at 10 kV in the samples

3 deposited during 1 h and 4 h.

4   The crystallographic structure was investigated by X-ray diffraction in grazing incidence

5 4º on a Brucker D8 Advanced system apparatus using Cu k_α radiation ($\lambda= 0.154$ nm) in the samples

6 deposited during 3h.

7

8 **2.2 Modulated IR Radiometry and determination of thermal parameters**

9   Thermal properties determination was performed using data obtained by Modulated IR

10 Radiometry (MIRR), a non-contact and non-destructive photothermal technique based on the

11 response from the materials to an intensity-modulated laser beam irradiation[1,10]. The created

12 "thermal waves" are then detected using an IR HgCdTe detector, connected to a two-phase Lock-

13 in amplifier (SR830), used to filter and amplify the small periodical variations of the detected IR

14 emission caused by the time and space small temperature oscillations occurring in the samples.

15 These small non-continuous oscillations allow us to separate the useful information from the high

16 radiation and temperature background around 300 K. Due to the frequency dependence "thermal

17 thickness" control, this technique is particularly suitable for studying thin films and coatings [1,2],

18 once depth resolved measurements of the thermal properties of thin films or coatings deposited on

19 thermally thick substrates can be done. Detailed information on the experimental setup can be

20 found elsewhere [11].

21   In order to interpret the signals measured for two-layer systems, like the ones studied here,

22 the in-phase and out-of-phase components of the modulated IR signals, giving information on the

23 thermal waves' amplitude and phase lag relative to the modulated excitation were measured by a

24 Lock-in amplifier. These measurements were normalised with the help of thermal wave signals

25 measured for a homogeneous opaque reference sample (sigradur®) under the same conditions.

26 This normalization eliminates all the frequency characteristics of the various components of the

27 measurement system.

28   The thermal diffusion time of the thin films, and the effusivity ratio of the coating/substrate

29 system can be obtained by applying the so-called "extremum method" [4]. These are fundamental

30 parameters to understand the role of heat diffusion and propagation on thin films and coatings.

31 According to this method, analytical solutions can be found for the relative extrema (i.e. minimum

1   or maximum) of the normalized phase (Φ_n) vs $(f\,/\mathrm{Hz})^{1/2}$. This results in unique solutions for the

2   *coating-to-substrate thermal reflection coefficient* (R_{cs}) and the coating's *thermal diffusion time*

3   (τ_c), as follows:

4     $$R_{cs} = \pm\sqrt{\frac{1-tan\theta}{1+tan\theta}}\,exp\theta \qquad\qquad (1)$$

5     $$\tau_c = \frac{\theta^2}{4\pi f_{extr}} \qquad\qquad (2)$$

6   where $\theta = \frac{1}{2}arcos\left(tan\Phi_{n,extr}\right)^2$ (3)

7   From equations (1-3), the thermal reflection coefficient (R_{cs}) and the thermal diffusion time

8   (τ_c) can be calculated directly from the measured quantities $\Phi_{n,extr}$ and f_{extr}, which represent the

9   minimum value of the normalized phase and the frequency at which the minimum occurs,

10   respectively. Once the thickness (d_c) of the films were independently measured by SEM, the

11   thermal diffusivity of the films can also be calculated[3]:

12    $$\alpha_c = d_c^2/\tau_c \qquad\qquad (4)$$

13   Finally, provided that the thermal effusivity of the substrate (e_s) is known, the thermal

14   effusivity of the film (e_c) can be calculated from the film to substrate effusivity ratio (R_{cs}):

15    $$R_{cs} = \frac{e_c-e_s}{e_c+e_s} \qquad\qquad (5)$$

16   The thermal diffusivity and effusivity of the coating are functions of its thermal

17   conductivity (k_c), density (ρ_c) and specific heat capacity (C_c). The product of these latter two

18   magnitudes $(\rho C)_c$ is the volumetric heat capacity of the coating, which can be calculated for the

19   coating together with its thermal conductivity using these expressions:

20    $$\alpha_c = \frac{k_c}{(\rho C)_c} \qquad\qquad (6)$$

21    $$e_c = \sqrt{k_c(\rho C)_c} \qquad\qquad (7)$$

22   It is worth mentioning that the coordinates of the extremum (f_{extr}, $\Phi_{n,extr}$) are not directly

23   obtained from the experimental data point with the lowest value of $\Phi_{n,extr}$. Instead, we performed

24   a fitting around the location of extremum using the general function $\Phi_n(f)$, which can be expressed

25   as:

26    $$\tan\Phi_n(f) = \frac{2R_{cs}exp\left(-2\sqrt{\pi\cdot f\cdot\tau_c}\right)sin\left(2\sqrt{\pi\cdot f\cdot\tau_c}\right)}{1-\left[R_{cs}exp\left(-2\sqrt{\pi\cdot f\cdot\tau_c}\right)\right]^2} \qquad\qquad (8)$$

1   This approach has two advantages. First, the error is reduced, since the extremum is located
2   by considering the shape of the curve and thus with several experimental data instead only one.
3   Second, the determination of f_{extr} is no longer restricted to the discrete values of frequency selected
4   for the experimental measurements, but it is obtained from the location of the extremum of the
5   fitting curve, which is not conditioned by the experimental conditions.

6

3. Results and discussion

3.1. Characteristics of the films

9   The characteristics of the deposition processes and the films are included in Table 1. The
10   values of pressure and voltage show a certain degree of drift during each deposition, which is
11   reasonable considering the duration of the deposition process. However, EDX measurements
12   carried out in the thinnest and thickest films are very similar, indicating that the chemical
13   composition of the films remains invariant through their thickness. Nevertheless, it can be noticed
14   a large overestimation of the N content by EDX for the film M, which was produced without any
15   introduction of O_2 nor N_2. This is pointed out by comparison with the RBS measurements carried
16   out on this sample (7% of O, and absence of nitrogen).
17   Figure 2 shows x-section SEM images of the three types of films (M, R, and P) deposited
18   at 1 and 4 hours. Both M and R samples have a columnar morphology characteristic from PVD
19   deposited films, as observed in the specimens grown for 1 h. The width of the columns decreases
20   with the increase of the flow of the reactive gas mixture (Figure 2a and b). The samples deposited
21   with the highest flow present a denser microstructure (Figure 2c). This evolution is very similar to
22   what has been reported by other authors[12,13]. For the samples deposited for 4h the evolution of
23   the microstructure is similar, but the samples identified previously as columnar tend to evolve to
24   a cone-like shape structure it the top part of the film. Huang et al also observed the formation of
25   this cone-shape microstructure for samples deposited during 2 h [14]. The sample in the poisoned
26   region still presents a dense microstructure. It is worth mentioning that many of the features of the
27   thicker films (e.g. columns) grow through the whole thickness of the film, despite the 3
28   interruptions suffered during the deposition due to the removal of the shields that protect the
29   substrates.

The characteristics of these films are in agreement with the three regions observed in previous works [5,6]. Thus, film M has metallic grey colour and it shows a clear metallic composition together with a XRD pattern composed by peaks of metallic α-Zr(ICCD 03-065-3366) (see Figure 3). Film R is golden, and it has a Zr/N ratio close to 1, with some addition of O (ca. 15 at. %). It is composed by sharp peaks of c-ZrN and c-Zr_2ON_2 (ICCD 03-065-7723 and 01-089-8345 respectively) (see Figure 3). Finally, film P, although chemically similar to the second, shows a Zr/N ratio more deviated from stoichiometry (1.3), and a higher O concentration (19 at. %). As a result, the structure is more amorphous, presenting broader peaks due to the distortion of the Zr-O-N lattice (see Figure 3).

3.2. Thermal properties

The experimental results presented herein refer only to the phase lag (Φ_n) vs. frequency (f) data from which the thermal parameters can be immediately determined, as explained in Section 2.2. Figure 4 shows the experimental data obtained for the inverse normalized phase lag vs modulation frequency for three different types of thin films deposited onto three different substrates with four different deposition times. The acquired experimental values and simulations according to the opaque-opaque two-layer model are represented by discrete symbols and solid lines, respectively.

The results are organized by showing the three different substrates (steel, silicon and glass) in rows and the three types of films (M, R and P) in columns. Films P become transparent for visible radiation as a consequence of the high O content. As a consequence, the results present deviations from the zero line of the inverse normalized phase lag (cf. Figs 4c, f and i). These results are not predictable from the theoretical model we are currently using, since it does not consider a high degree of semi-transparency of the film. A generalization of the theoretical model, including the semi-transparency approach, is underway.

In each of the 9 substrate-film intersections there are 4 sets of data that represent films with deposition times between 1 and 4 hours. In that regard, according to Eqs.1-5, if we consider a pure variation of film thickness (d_c) while keeping the film and substrate parameters invariant, we should expect a shift of the position of the extremum (f_{min}) towards higher values (caused by the reduction of τ_c), but not a change in the value of $\Phi_{n,min}$. This is quite the case in few cases in Figure 4 (see e.g. Fig. 4c), although this is not the general behavior. In contrast, it is much more common

1 that the height of the extreme is also changed (see for instance Fig. 4a), which indicates a variation

2 of the thermal properties of the film for different thicknesses. In addition, in some of the samples,

3 it was not possible to find a clear minimum or maximum (films R1 and P1 on steel, P1 on silicon

4 and films P on glass). Further, uncommon narrow shapes of the plots have been identified in two

5 cases (films M1 on silicon and R4 on glass). These behaviors can be related with issues during

6 measurement or adhesion problems. Therefore, although the fitting results and thermal properties

7 of all the films are summarized in Table 2, the data from these samples found clearly out of range

8 has been excluded from the plots of the behavior of the thermal properties of the films depending

9 on their thickness, which are depicted in Figure 5.

10   The main general observation is that there is much lower dispersion in the results of the

11 films P (right column in Fig. 5) than in those obtained for films M and R. It is worth mentioning

12 that such effect cannot be attributed to the exclusion of the films P deposited on glass, since the

13 dispersion of data considering only films deposited on silicon and steel is still much higher for

14 films M and R. This result is likely connected to the different nature of the films; thus, films M

15 and R are crystalline and show a clear columnar growth, while films P are amorphous and much

16 denser. As a consequence, this latter film seems to grow similarly onto different substrates and to

17 show similar properties regardless of the thickness. In other words, little microstructural variation

18 is observed for this film (the film is 'always the same').

19   The values of effusivity ratio (e_c/e_s) for films deposited on steel and silicon are lower than

20 1, and the opposite is observed in case of glass (cf. top row in Fig. 5). This is expected due to the

21 different nature of the substrates in comparison with the films, and in agreement with the type of

22 extremum (minimum or maximum) observed in Figure 4. The values are not constant, indicating

23 that the thermal properties of the film will depend on the substrate and the thickness of the film.

24 The trends of thermal diffusivity, conductivity, and volumetric heat capacity of the coating (α_c, k_c,

25 and (ρC)$_c$) with film thickness are similar for the three films, although clearer for films M and R

26 than for P ones, probably due to the reasons explained above. In general, k_c and α_c show a growing

27 trend with film thickness, while the opposite is seen for (ρC)$_c$; in all the cases, a kind of 'steady

28 state' is reached for the thickest films. The reason for this 'stabilization' is likely due to the

29 microstructural evolution of the films, which is has more weight when changing from 1 h to 2 h

30 of deposition time (thickness increases by ca. 100%) than when changing from 2 to 3 h (increase

31 of ca. 50%) or from 3 to 4 h (increase of ca. 33%). In other words, the film moves towards a 'bulk'

1   state, but the rate of variation of film properties reduces. The increase of thermal conductivity can

2   be well explained in terms of microstructural variation (improved interconnection, filling of

3   spaces), while the reduction of volumetric heat capacity could be related to the reduction of density

4   for thicker films (larger voids and large column separation). Wei et al. [15], reported an exponential

5   increase of α for different substrates. This behavior was also observed in some cases, e.g. films M

6   on steel (linear behavior on Fig. 5d, notice the logarithmic y axis). These authors address other

7   two factors to explain this trend. First, the presence of interfacial thermal resistance caused by the

8   mismatch in thermal conductivity between film and substrate, which alters the heat flow and the

9   resultant α of the combined system. This effect would be reduced for higher film thickness, due to

10   the annealing effects caused by longer duration of deposition. Second, the presence of grain

11   boundaries in microstructured thin films can cause scattering of the phonons, which carry the

12   thermal energy. This effect will be reduced in in thicker films due to the coalescence of grains.

13   Beyond the general observed trends, a certain dispersion of data is observed when

14   comparing results of films on different substrates (i.e. different values may be obtained for a certain

15   film with a certain thickness in different substrates). However, it seems that such dispersion

16   decreases with thickness of the films. This can be easily observed for films R (cf. e.g. Fig. 5e).

17   This can be also appreciated for the films M, although the films M2 and M3 on Si show values

18   that seem out of the trend, likely connected to the noisy results in Fig. 4d. The reason for the

19   reduction of data dispersion with thickness likely reflects that thin films are more influenced by

20   substrate (e.g. different types of film growth, wetting, etc.), but that influence gets reduced when

21   the thickness increases.

22   The value of α_c for the films M is ca. 10^{-6} m^2/s, which fits very well with values found for

23   Zr thin [16] and also for bulk Zr (12.4×10^{-6} m^2/s), since for metallic thin films the thermal

24   diffusivity values are typically one order of magnitude below those corresponding to the bulk

25   material. The values of α_c in steel are in agreement with other results Zr-O-N films[11,17]. In fact,

26   it is observed that α_c varies from ca. 10^{-6} to 5×10^{-7} m^2/s when changing the nature of the film from

27   M to R to P (considering the 'steady state' values), in excellent agreement with the results

28   previously reported [17]. The values of k_c indicate low thermal conductivity, probably related with

29   the columnar microstructure of the films. However, the values of the P film are lower than M and

30   R (considering the steady state values), in agreement with the chemical nature of the films (metals

vs. ceramic). The values obtained for $(\rho C)_c$ are also in the good range, which is supposed to be between 10^6 and 10^7 J/m^{3}K [1].

4. Conclusions and outlook

A systematic study of thermal properties of Zr-O-N thin films was carried out, using a modulated IR radiometry. Three sets of films were used: metallic type (M); oxynitride reactive type (R) and oxynitride poisoned type (P). The films of each one of these sets had the same composition (deposited in the same batch), but they were deposited on three different substrates and four different thicknesses in each type of substrate. This systematic study allowed us to test the accuracy of the Extremum method when varying different experimental parameters.

In general, the results have been quite satisfactory, and the different observations have been successfully explained based on the phase and microstructural characteristics of the films. P shows a much lower dispersion of data, as a consequence of its amorphous nature and dense growth, in opposition to films M and R. These two films show a variation of thermal properties with the thickness of the film that could be addressed in terms of microstructural variation (e.g. better columnar interconnection). Additionally, the dispersion of data among substrates was higher at lower thickness, probably due to higher influence of substrate (e.g. growth type and wetting). Finally, the values of the thermal parameters are in agreement with results from literature, and in line with the chemical nature of the films.

References

[1]   D.P. Almond, P. Patel, Photothermal Science and Techniques, Springer, 1996.

[2]   F. Macedo, A. Gören, F. Vaz, J.L. Nzodoum Fotsing, J. Gibkes, B.K. Bein, Photothermal characterization of thin films and coatings, 82 (2008) 1461–1465. doi:10.1016/j.vacuum.2008.03.007.

1   [3]   M. Apreutesei, C. Lopes, J. Borges, F. Vaz, F. Macedo, Modulated IR radiometry for
2   determining thermal properties and basic characteristics of titanium thin films, J. Vac. Sci.
3   Technol. A Vacuum, Surfaces, Film. 32 (2014) 41511. doi:10.1116/1.4884351.
4   [4]   J.L.N. Fotsing, J. Gibkes, J. Pelzl, B.K. Bein, Extremum method: Inverse solution of the
5   two-layer thermal wave problem, J. Appl. Phys. 98 (2005) 63522. doi:10.1063/1.2058180.
6   [5]   C.I. da Silva Oliveira, D. Martinez-Martinez, A. Al-Rjoub, L. Rebouta, R. Menezes, L.
7   Cunha, Development of a statistical method to help evaluating the transparency/opacity of
8   decorative thin films, Appl. Surf. Sci. 438 (2018) 51–58. doi:10.1016/j.apsusc.2017.10.017.
9   [6]   C.I. da S. Oliveira, D. Martinez-Martinez, L. Cunha, M.S.S. Rodrigues, J. Borges, C. Lopes,
10   E. Alves, N.P.P. Barradas, M. Apreutesei, C.I. da Silva Oliveira, D. Martinez-Martinez, L.
11   Cunha, M.S.S. Rodrigues, J. Borges, C. Lopes, E. Alves, N.P.P. Barradas, M. Apreutesei,
12   Zr-O-N coatings for decorative purposes: Study of the system stability by exploration of the
13   deposition parameter space, Surf. Coatings Technol. In Press (2018) 1–8.
14   doi:10.1016/j.surfcoat.2017.11.056.
15 [7]   N.P. Barradas, C. Jeynes, R.P. Webb, U. Kreissig, R. Grötzschel, Unambiguous automatic
16   evaluation of multiple Ion Beam Analysis data with Simulated Annealing, Nucl.
17   Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 149 (1999)
18   233–237. doi:10.1016/S0168-583X(98)00731-9.
19 [8]   N.P. Barradas, C. Pascual-Izarra, Double scattering in RBS analysis of PtSi thin films on
20   Si, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 228
21   (2005) 378–382. doi:10.1016/j.nimb.2004.10.074.
22 [9]   N.P. Barradas, M.A. Reis, Accurate calculation of pileup effects in PIXE spectra from first
23   principles, X-Ray Spectrom. 35 (2006) 232–237. doi:10.1002/xrs.
24 [10] C.A. Bennett, R.R. Patty, Thermal wave interferometry: a potential application of the
25   photoacoustic effect, Appl. Opt. 21 (1982) 49–54. doi:10.1364/AO.21.000049.
26 [11] J. Gibkes, F. Vaz, a C. Fernandes, P. Carvalho, F. Macedo, R.T. Faria, P. Kijamnajsuk, J.
27   Pelzl, B.K. Bein, Analysis of multifunctional oxycarbide and oxynitride thin films by
28   modulated IR radiometry, J. Phys. D. Appl. Phys. 43 (2010) 395301. doi:10.1088/0022-
29   3727/43/39/395301.
30 [12] S.C. Ferreira, E. Ariza, L.A.A. Rocha, J.R.R. Gomes, P. Carvalho, F. Vaz, a. C.C.
31   Fernandes, L. Rebouta, L. Cunha, E. Alves, P. Goudeau, J.P.P. Rivière, Tribocorrosion
32   behaviour of ZrOxNy thin films for decorative applications, Surf. Coatings Technol. 200

1   (2006) 6634–6639. doi:10.1016/j.surfcoat.2005.11.083.

[13] J.-H. Huang, T.-H. Wu, G.-P. Yu, Heat treatment induced phase separation and phase transformation of ZrNxOy thin films deposited by ion plating, Surf. Coatings Technol. 203 (2009) 3491–3500. doi:10.1016/j.surfcoat.2009.05.016.

[14] J.-H. Huang, Y.-Y. Hu, G.-P. Yu, Structure evolution and mechanical properties of ZrNxOy thin film deposited on Si by magnetron sputtering, Surf. Coatings Technol. 205 (2011) 5093–5102. doi:10.1016/j.surfcoat.2011.05.015.

[15] P.C. Wei, H.C. Shih, S. Chattopadhyay, C.M. Hsu, F.S. Lin, K.H. Chen, A. Ganguly, L.C. Chen, Thermal diffusivity study in supported epitaxial InN thin films by the traveling-wave technique, J. Appl. Phys. 104 (2008). doi:10.1063/1.2986314.

[16] A. Mandelis, ed., Progress in Photothermal & Photoacoustic Science & Technology, Vol 1 Principles and perspectives of photothermal and photoacoustic phenomena, Elsevier, New York, 1992.

[17] F. Macedo, P. Carvalho, L. Cunha, F. Vaz, J. Gibkes, B.K. Bein, J. Pelzl, F. Macedo, P. Carvalho, B.K. Bein, J. Pelzl, The Role of Modulated IR Radiometry Measurements in the Characterization of Zr-O-N Thin Films, Plasma Process. Polym. 6 (2009) S760–S766. doi:10.1002/ppap.200931802.

Figures captions

Figure 1. a) Representation of the deposition chamber setup. 1 – Magnetron head, 2 – Target, 3- Substrate holder, 4 – Cover; 5- Substrates (glass, steel and silicon pieces). b) Scheme of the growth of films with different thickness by exposing the substrates to different deposition times (1, 2, 3 and 4 hours). The indexes I, II, III and IV represent growth occurring during the first, second, third, and fourth hours of deposition, respectively.

Figure 2 .X-section SEM images of different Zr-O-N films. a) M1. b) R1. c) P1. d) M4. e) R4. f) P4. All the scale bars represent 500 nm.

Figure 3. X-ray diffraction of representative films of each type and respective phase identification. For the film M, an inset is included to zoom in the peaks with lower intensity.

Figure 4. Inverse calibrated IR phase lag signals measured for three types of films (M, R and P), on three different substrates (steel, silicon and glass) with four different deposition times. The points and solid lines correspond to experimental measurements and the opaque two-layer approximations (Eq. 8), respectively.

Figure 5. Thermal parameters of the different samples obtained from the fittings of the experimental results with the two layers model represented in Figure 4 using Equations 1-8. The black dashed lines represent guides for the eye.