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Mechanical and decorative properties of ZrO_x thin films prepared by reactive-magnetron sputtering

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Within the frame of this work is zirconium oxide - ZrO_x decorative thin films were deposited by reactive magnetron sputtering. These films have been characterized in terms of some proprieties as films colour, mechanical properties, thickness and composition, taking into account the influence of certain deposition parameters such as: reactive gas flow (O_2) and deposition time. Regarding the composition, the obtained films are characterized by two zones, one rich in Zr which leads to various metallic colours of the films and the second zone rich in O_2, which lead to some interference colour of the films. The hardness increase with the increase of reactive gas flow until 15 GPa for ZrO_x coatings deposited at 200^0 C.

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1. Introduction

Zirconium oxide (ZrO_x) films have wide applications in optical fields [1] including high-reflectivity mirrors, broadband interference filters, wave guides with small losses and active electro-optical devices [2], due to their excellent properties such as high refractive index and high transparency in the 0.3–8 µm range. ZrO_x crystallizes in three distinct polymorphs depending on the temperature and pressure conditions. The monoclinic phase is stable at room temperature; the tetragonal phase is stable from 1170 to 2370^0 C and cubic phase stability region is 2370 – 2680^0 C [3].

Furthermore, Zr is used to enhance the dielectric behaviour of different oxides such as lead, barium, and strontium oxides. Possessing high dielectric permittivity, such materials can find application in the fabrication of memory units and next-generation metal–oxide–semiconductor field-effect transistors. Thin films differ in properties from bulk materials [4]. In addition, ZrO_x is a promising candidate to replace silicon dioxide as gate dielectric in transistors.

This wide range of interesting applications has led to numerous efforts to synthesize zirconium oxide layers, using a number of different techniques, including electron beam evaporation, ion-assisted deposition, pulse laser deposition and sputtering [5-8].

The PVD technique reactive d.c. magnetron sputtering, which is studied here, has the advantage over several other techniques listed above that it can be easily scaled from small sized laboratory targets to industrial applications on large area substrates such as the coating of architectural glass.

Reactive magnetron sputtering is a deposition technique, which allows a good control of the mechanical (hardness, elastic modulus, residual stresses, adhesion) and physical (crystalline aspect) properties. The reactive sputtering deposition is a very attractive process to elaborate metallic oxides with good uniformity [9].

The properties are dependent on the film's chemical composition, and microstructure, which are closely correlated with the deposition technique and parameters. Other properties such as high hardness, large resistance against oxidation, make the ZrO_x thin films interesting as a mechanical applications material [10].

In the present work, we investigate the influence of deposition parameters on the film composition, decorative and mechanical properties. The films have been prepared using different oxygen (O_2) flow rates by d.c. reactive magnetron sputtering technique.

2. Experimental details

The ZrO_x films were deposited by d.c. reactive magnetron sputtering system from high purity Zr (99.6 at. %) target onto polished stainless steel substrate - samples (AISI 316) ~ 0.5 mm thick for residual stresses analysis, standard Si (100) substrate - samples for composition analysis and glass substrates - samples (~ 1.2 mm) used for decorative aspects characterization. Films were prepared in static mode (substrates to be coated were fixed in front of the target), using a gaseous atmosphere composed of argon and oxygen with a base pressure in the deposition chamber ~ $5x10^{-3}$ mbar, using constant values of temperature (200^0 C).

Prior to depositions, the substrates were sputter etched for 1200 s with 60 sccm constant Ar flow at 200 kHz frequency, with $t_{on} = 1.536x10^{-6}$ s and 0.6 A current. In situ cleaning is done in the deposition system in order to remove the small amounts of contamination that have developed since the primary cleaning process.

The deposition processes supposed a reactive gas flow, which varied from 1 to 15 sccm, with a total pressure around $5x10^{-3}$ mbar and deposition times between 3000 and 3600 s.

The substrates were heated at $T_s=200^0$ C using d. c. bias grounded, with a current of 2 A. Argon flow was kept constant at 60 sccm.

The substrate rotation used was 7 rpm with the substrate holder positioned at 65 mm in all runs. Evolution of temperature was monitored with a thermocouple placed close to the surface of the substrate holder. The experimental parameters are presented in table 1.

Table 1. Experimental parameters used for ZrO_x films.

Samples	O_2 flow [sccm]	Deposition time [s]	Thickness (nm)
ZO 1	1	3000	1800
ZO 2	1.5	3000	1700
ZO 3	2	3000	2000
ZO 4	2.5	3000	1800
ZO 5	3	3000	2100
ZO 6	4	3600	2300
ZO 7	5	3600	2500
ZO 8	6	3600	2500
ZO 9	9	3600	230
ZO 10	15	3600	200

Atomic composition of the deposited samples was measured by Rutherford Backscattering Spectroscopy (RBS). The characterization of film's colour was obtained with a commercial MINOLTA CM-2600d portable spectrophotometer (wavelength range 400-700 nm). Colour specification was computed under the standard CIE illuminate D65 and represented in the CIELAB 1976 colour space. The thickness was measured using a scanning electron microscope (SEM).

The residual stress values, σ_r, were determined from Stoney equation [11] using substrate curvature radii, both before and after coating deposition [12]. The hardness experiments were carried out in a Fischerscope H100 ultra-micro-hardness tester equipped with a Vickers diamond indenter.

The applied load was increased in 60 steps (the same for unloading) until the nominal load reached the value of 30 mN (maximum load in all tests). The system has a load resolution exceeding 1 µN and the range of the nominal test load is between 4 mN and 1 N. The indentation depths were obtained with an accuracy of 2 nm. The measurements of hardness were determined on representative coatings from the both zones. Investigation of stainless steel substrates (discs with 25 mm diameter) was made to determinate the values of elastic modulus of the films. The coatings were measured with a high precision co-ordinate measuring system – LC 2100 equipped with a laser tip and having a resolution of about 0.5 µm. During the measuring procedure, the tip force in contact with the samples is weak enough (~ 20 µN) and thus does not affect the coordinate result.

3. Results and discussion

3.1. Deposition rate and composition

The reactive gas flow and the thickness of the produced coatings are presented in table 3.

Fig. 1 shows the dependence between deposition rate and reactive gas flow, of as produced ZrO_x films. From figure 1 it can be observed that the evolution of the deposition rate as a function of reactive gas flow can be divided in two different regimes. In first regime, corresponding to the samples deposited with the reactive gas flow below 8 sccm, the deposition rate has a stabilization where the obtain values are roughly $6x10^{-2}$ nm/s.

In second regime there is a decrease of the deposition rate with the increase of the reactive gas flow from ~ $6.9x10^{-2}$ nm/s to the lowest value of the deposition rate (~ $0.5x10^{-2}$ nm/s) corresponding to the ZrO10 sample with 200 nm thickness.

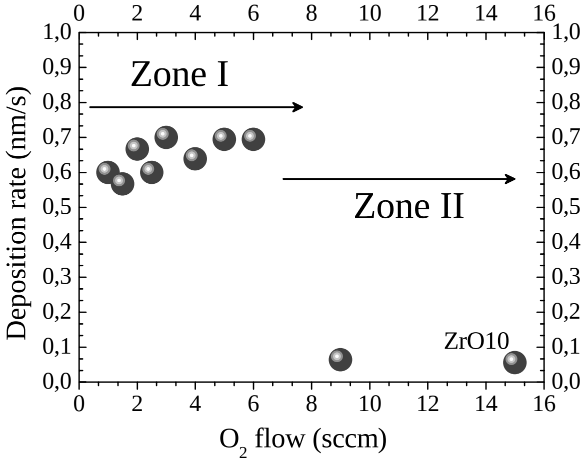

Fig. 1. Deposition rate of the produced ZrO_X coatings as function of the gas flow rate.

Observing Fig. 2, where is presented the variation of the atomic concentration of elements as function of the reactive gas flow one first conclusion may be pointed out: I) the global increase of the oxygen content with the increase of reactive gas flow.

According with Fig. 1, the represented values confirm and clears out again the two different zones division, which are the same like in deposition rate plot. Zone I is clearly definite, with oxygen flow from 1 to 8 sccm and deposition rates with values from ~ $6x10^{-2}$ nm/s to ~ $6.9x10^{-2}$ nm/s.

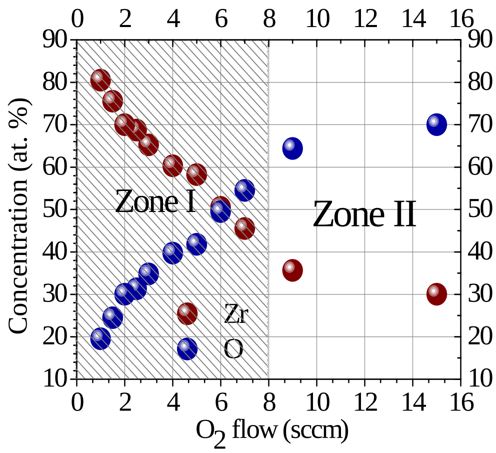

Fig. 2. Variation of elemental concentration as function of the gas flow.

Samples from Zone I (prepared with an amount of reactive gas flow below 8 sccm) present an increase of the oxygen content to ~ 60 at. %, while the amounts of zirconium systematic decrease from the highest value ~ 80 to ~ 35 at. %. Moreover, the amount of zirconium has a stable value at ~ 70 at. %. In this region the amount of zirconium is higher compared to the amount of oxygen which is relatively low (~ 20 at. %).

Regarding to samples from Zone II it can be seen that the amount of oxygen is increasing slowly and it's stable at ~ 70 at. %. Also, the amount of zirconium is decreasing smoothly and it begins to stabilize at ~ 30 at. %.

3.2. Colour

The variation of the colour coordinates of the CIE Lab colour space [13] as function of the oxygen flow is represented in figure 3.

All samples have a relatively high L* value, and a* and b* coordinates are close to zero in zone I were samples have a metallic colour because of the high values of brightness (L*) which are determined by interactions between incident photons and free electrons. Regarding the chromaticity coordinates the distinction between the two zones is again quite clear. When the flow rate increases from 0 to 8 sccm (samples from zone I) the values of a* and b* show no significant changes.

The films colour changed from the metallic colour to interference colour in zone II (sample deposited with a flow rate from 8 to 15 sccm). Over a flow rate of 8, L* maintains always between 60 and 70, but a* decrease to -15 and then increase again to -3. Moreover, the second chromatic coordinate b*, have an increasing evolution between 40 and 62.

The samples with the highest value of oxygen present the best colorimetric characteristics. This behaviour was already observed in a different set of samples produced by the authors using other deposition methods like filtered cathodic vacuum arc [14-18].

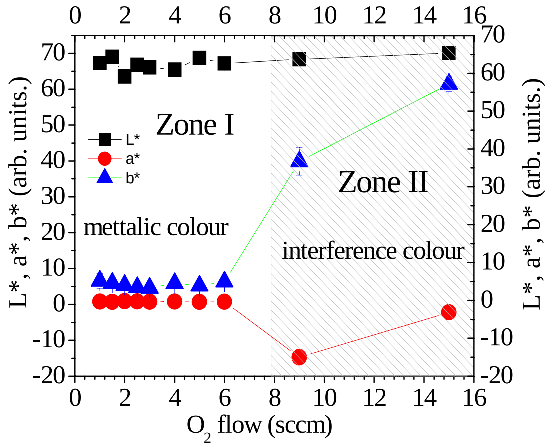

*Fig. 3. Variation of the colour coordinates, L*a*b*, of ZrO_x coatings as function of gas flow.*

3.3. Mechanical characterization

3.3.1 Hardness and Young's modulus

Fig. 4 shows the evolution of the hardness and elastic modulus as function of reactive gas flow. From this graph it can be seen that all the coatings present loading and unloading curves that are approximately parabolic. This is a good indication that the deformation in the elastic regim is significant. In Zone I, it is known the increase in hardness of the coatings, varying from ~ 8 up to ~ 15 GPa. This initial increase is then followed by a systematic decrease of the film property, reaching value of 10 GPa of the sample prepared with 9 sccm where is already Zone II. Moreover, it is possible to observe that within Zone II there is a smoother decrease in hardness values, if compared to what happens in Zone I. In terms of the main features that may explain this particular behaviour of hardness, it is important to state that, first of all, this evolution is well correlated with the structural evolution. In Zone II, it can be seen the decrease in hardness values, varying from ~ 10 GPa down to ~ 9 GPa.

The Young's modulus (elastic modulus) values are presented in figure 4. It has to be underlined that this parameter has a similarly behaviour in evolution with the hardness. The elastic modulus presents also an initial increase in the first compositional and structural zone, followed by a smoother decrease in Zone II. The Young's modulus values from Zone I, varying from ~ 210 GPa up to ~ 250 GPa and in Zone II from ~ 240 GPa down to ~ 230 GPa.

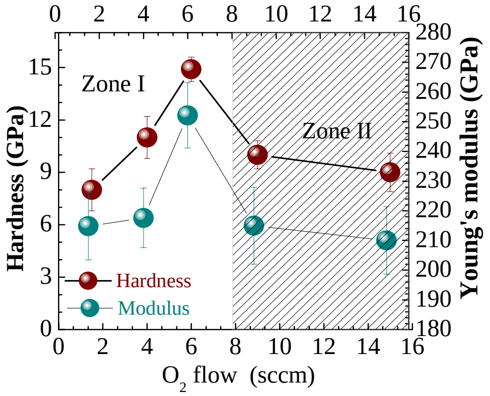

Fig. 4. Evolution of hardness and elastic modulus as function of reactive gas flow.

3.3.2 Residual stress

Fig. 5 shows the evolution of residual stresses as a function of reactive gas flow. From this graph it can be seen that coatings from Zone I have zero stress because the values are very close to the zero value. Coatings from Zone II presents compressive stress state because the crystallographic structure ZrO_2 is present in this zone. The relationship between these residual stresses, the microstructure, composition and the deposition conditions of thin films deposited by PVD methods has been the subject of active investigation for many years [19-20]. Through a complete fundamental understanding of the physical mechanisms involved is still lacking, a large columnar growth - type structure in all samples [21], lying in the transition between T and I zones in Thornton's [22].

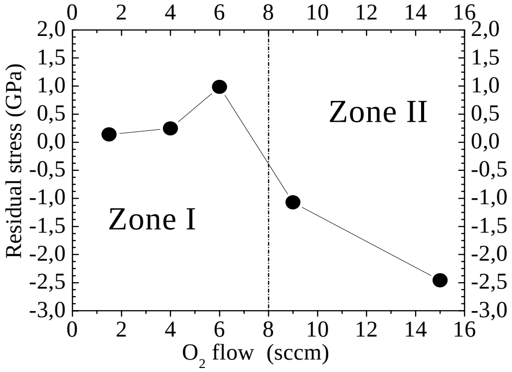

Fig. 5. Evolution of residual stress as function of reactive gas flow.

Fig. 6 presents the evolution of hardness as a function of residual stress. The highest hardness value is corresponding to ZrO8 sample (~ 0.98 GPa) and the lowest value (~ 0.13 GPa) to ZrO2 sample. Both films are situated in Zone I where the coatings are in the zero stress state.

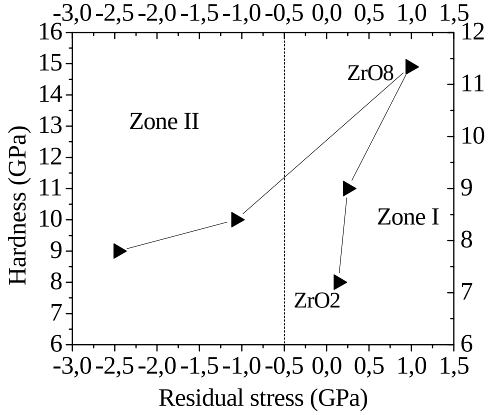

Fig. 6. Evolution of hardness as function of residual stress.

Fig. 7 shows the evolution of Young's modulus and residual stresses as a function of hardness. It is clearly the mirror evolution of the two parameters (Young's modulus and residual stress) and that the values of ZrO8 and ZrO2 samples remain the same like in figure 5 and 6: the lowest ZrO2 sample with ~ 210 GPa value of elastic module and ~ -2.5 GPa residual stress, and the highest ZrO8 with ~ 250 GPa value of elastic module and ~ 1.5 GPa residual stress.

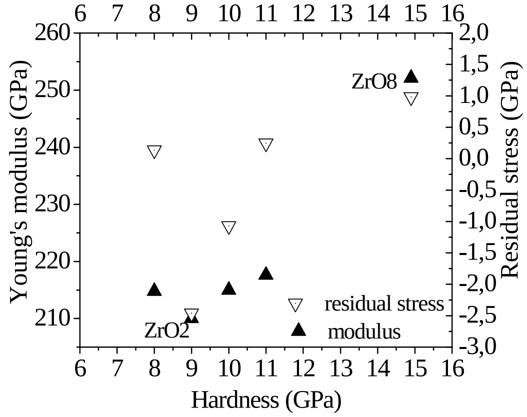

Fig. 7. Evolution of Young's modulus and residual stress as a function of hardness.

4. Conclusions

The experimental data presented above offer an image of the reactive sputter deposition of zirconium oxide. The compositions, optical and mechanical properties of ZrO_2 films deposited by the reactive magnetron sputtering technique have been investigated at varying O_2 flow rates. The O_2 flow rate is found to be an important parameter in controlling the film composition and properties. One important fact is that during the experimental work all 10 coatings presented different evolution, but the two regimes (Zone I and Zone II) remain clearly definite even if we use different characterization techniques. The film composition presents two zones, one rich in zirconium content (Zone I) which leads to various metallic colours of the films and the second zone rich in oxygen content (Zone II), which lead to some interference colour of the films. The hardness increase with the increase of reactive gas flow content until reaches 15 GPa for ZrO_x coatings deposited at 200^0 C. Coatings from Zone II are in a compressive stress state.

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