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DECORATIVE ASPECTS OF ZrN_x THIN FILMS PREPARED BY REACTIVE MAGNETRON SPUTTERING

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Abstract: *Zirconium nitride films were deposited by direct current (d.c.) reactive magnetron sputtering at the substrates temperature of 200 °C in an* N_2 *and Ar ambient. In terms of composition and optical properties that defines the decorative aspects of the thin films it can be observed three different zones. The first one riched in Zr (max. 5 sccm for* N_2 *flow), the second zone rich in Zr and* N_2 *(for* N_2 *flow between 5 and 15 sccm), and the last one rich in* N_2 *(for* N_2 *flow between 15 and 45 sccm). According to the results, the films that belong to the first region exhibited metallic colors, the second region exhibited several brown colors, and the third region with more nitrogen shows a dark blue color.*

Key words: *ZrN_x thin films, reactive sputtering, properties, decorative coatings, composition.*

1. Introduction

Transition metal nitride coatings, mainly based on titanium, chromium and zirconium, are used as protective coatings against wear and corrosion. Zirconium nitride is an attractive material due to its good chemical and physical properties [2], [10], [13], [17]. It has high chemical and thermal stability and high hardness and abrasion resistance, and it might be suitable for making thin-film resistors with high resistance. It is not only applied as Josephson junctions, diffusion barriers, cryogenic thermometers, and hard coatings, but also applicable to thermal point heads, metal-based transistors, and three-dimensional integrated circuits [8], [9], [15].

In addition, these nitrides may exhibit an interesting, but limited, range of colors (golden yellows, different shades of grey, and black tones) allowing them to be used as decorative coatings [1], [4], [14].

The ZrN_x films have can be prepared by a variety of techniques including chemical vapour deposition (CVD), reactive sputtering, pulsed laser deposition, and ion-assisted deposition. Among these methods, direct current (d.c.) reactive magnetron sputtering is the most commercially practiced method because of its various advantages like high deposition rates on larger area substrates, control of the film composition, small substrate temp rise during film deposition, films with better adhesion and thickness uniformity [3].

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Reactive magnetron sputtering is a deposition technique allowing a good control of the mechanical (hardness, elastic modulus, residual stresses, and adhesion) and physical properties such as crystallinity.

In this article, we presented an experimental study of the decorative proprieties of sputtered ZrN_x films.

2. Experimental Procedure

The ZrN_x thin films were deposited by direct current (d.c.) reactive magnetron sputtering in home made system from high purity Zr (99.6 at. %) target onto polished stainless steel ~0.5 mm thick, used for residual stresses analysis, standard silica, used for composition analysis and glass substrates (~1.2 mm) used for decorative proprieties characterization.

Films were prepared in static mode (substrates to be coated were fixed in front of the target), using a gas atmosphere composed of argon and nitrogen with a base pressure in the deposition chamber of $\sim 5\times10^{-3}$ mbar using constant values of temperature 200 °C. Prior to depositions, the substrates were etched for 1200 s with 60 sccm constant Ar flow at 200 kHz frequency, with $T_{on} = 1.536\times10^{-6}$ and 0.6 A current. In situ cleaning is done in the deposition system with intension to remove the small amount of contamination that has developed since the primary cleaning process [6], [11], [16].

In Table 1 are presented the principal parameters used for etching.

Table 1

Experimental parameters used for etching

Parameter	Value
Argon flow (sccm)	60
Current (A)	0.6
Frequency (kHz)	200
T_{on} (s)	1.536×10^{-6}
Duration (s)	1200

Reactive gas flows varied from 2 to 40 sccm, with a total pressure around 5×10^{-3} mbar and deposition times between 2400 and 4000 seconds. The substrates were heated at T_s = 200 °C using a grounded substrate bias. Argon flow was kept constant at 60 sccm.

The rotation of the substrate 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 [5], [7], [12].

The experimental parameters are presented in Table 2.

Atomic composition of the deposited samples was measured by Rutherford Backscattering Spectroscopy (RBS).

The characterization of film's color was represented under the standard CIE illuminant D65 and represented in the CIELAB 1976 colour space. The characterization of films colour was represented in the CIELab 1976 colour space by using a commercial Minolta CM-2600d portable spectrophotometer (wavelength range: 400-700 nm), with

Experimental parameters used for deposition Table 2

Parameter	Probe	ZN1	ZN2	ZN3	ZN4	ZN5	ZN6	ZN7	ZN8	ZN9	ZN10	ZN11
N_2 flow [sccm]		2	4	5	5.5	6	7	8	10	20	30	40
Deposition time [s]		2400	2400	3000	3000	3600	3600	3600	3600	3600	4000	4000
Substrate bias		Grounded										
Argon flow [sccm]		60										
Total pressure [mbar]		$\sim 5\text{x}10^{-3}$										
Current [A]		2										
Tension [V]		306	314	318	337	341	337	337	341	349	349	349

diffused illumination (D65 light source) at an 8° viewing angle (specular component included). This equipment is equipped with a 52 mm diameter integrating sphere and 3 pulsed xenon lamps. The observer was placed at a 10° angle [15]. The thickness was measured using a Leica Cambridge S-360 SEM equipped with a fully automated stage, with a maximum travel of 100 mm in the *X* and *Y* axes, and 50 mm in the *Z* axis.

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. In Figure 1 is represented the deposition rate of produced ZrN_x films as function of the reactive gas flow.

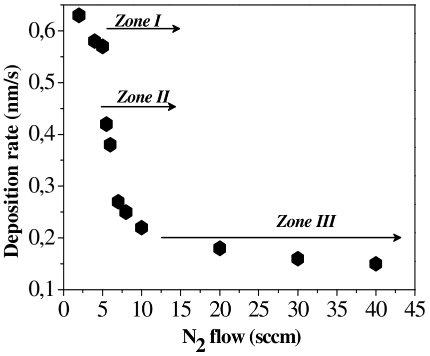

Fig. 1. *Deposition rate of the produced* ZrN_x *coatings as function of the gas flow rate*

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 three different regimes. In the first regime, corresponding to the samples deposited with reactive gas flow between 2 and 5 sccm there is a continuous decrease of the deposition rate from 0.63 nm/s to 0.57 nm/s.

In the second regime (gas flows between 5.5 and 10 sccm) there is still a decrease of the values of this parameter, where the obtained values are between 0.42 nm/s to 0.22 nm/s.

In the last region, the gas flow increased from 20 to 40 sccm there is almost a stabilization of the deposition rate from 0.18 nm/s to 0.15 nm/s.

In Table 3 are presented the values of thickness of ZrN_x films.

Table 3

Reactive gas flow rate during depositions and thickness of ZrN_x *films*

Samples	Thickness [mm]	Flow [sccm]
ZrN1	1.5	2
ZrN2	1.4	4
ZrN3	1.7	5
ZrN4	1.4	5.5
ZrN5	1.0	6
ZrN6	0.90	7
ZrN7	1.25	8
ZrN8	0.80	10
ZrN9	0.65	20
ZrN10	0.65	30
ZrN11	0.58	40

Figure 2 presents the variation of atomic concentration as a function of the reactive gas flow. As it can be observe the figure confirms the presence of the three different zones that separate the coatings. Zone I (prepared with an amount of reactive gas flow below 5 sccm) reveals a suddenly increase of the nitrogen content to ~45 at. % while the content of zirconium decrease from

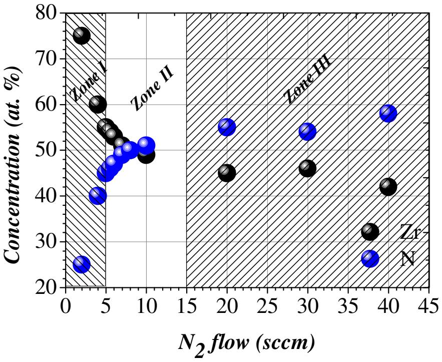

Fig. 2. *Variation of atomic concentration as a function of the reactive gas*

the highest value (~75 at. %) to ~55 at. %. Zone II (prepared with an amount of reactive gas flow below 10 sccm) presents a smoother increase of the amount of nitrogen to ~51 at. % and the amount of zirconium are decreasing to a value of ~49 at. %. Regarding to samples from zone III it can be seen that the amount of nitrogen is increasing to 58 at. % while the content of zirconium is decreasing to a value of ~42 at. %.

3.2. Color Characterization of the Coatings

From the Figure 3, it can immediately conclude that again, there is a notorious consistency in the obtained results, where the same three regions are still present.

The Figure 3 shows the zone I (from 2 to 5 sccm) corresponds to high values of brightness L^*, and have a colour that varies from metallic gray to a golden yellow. Zone II corresponds to the lower values of brightness, with colors from brown to dark brown. Zone III presents almost stable values of brightness, with dark blue colors.

In order to understand this differences between the samples of these three zones, one must keep in mind that the brightness of metallic materials is determined by interactions between incident photons and free electrons.

In Figure 4 where is presented the chromaticity coordinates (a^* and b^*) of the CIELAB 1976 colour space. For zone I where the flow of nitrogen is less, the values of chromaticity coordinates are showing an increase of a^* and b^* (yellowness). The colour of the samples are changing from a very bright pale-yellow to a golden but with an increase of the yellowness (increase of the positive value of b^*). In zone II we have values of a^* that are almost stable but for b^* we have a significantly increase, meaning that the colour of the samples changed from golden (5.5 sccm) to an almost dark brown (10 sccm). Zone III presents a decreasing of a^* and b^* values, these means that samples have dark colors, going from dark brown (10 sccm) to a dark blue (40 sccm).

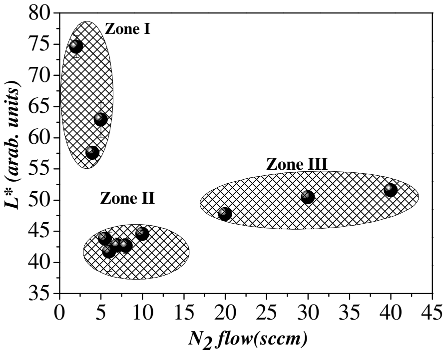

Fig. 3. *Brightness coordinate L^* of the CIELAB 1976 colour space for all the samples. The error bar was determinate by maximum deviation to the average value*

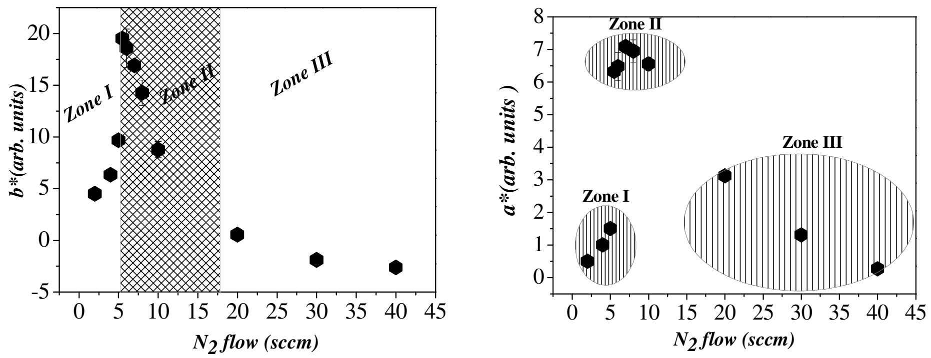

Fig. 4. *Chromaticity coordinates (a^* and b^*) of the CIELAB 1976 colour space, under the standard CIE illuminant D65*

In Figure 5 is presented the coordinate of the chromaticity (a^* and b^*) and the brightness (L^*) so that it can bee seen the differences between them.

Zone I reveals the higher values of brightness and an increase of chromaticity values because of the zirconium high content. Because of all that, films in this zone present several metallic colors.

In zone II where the films present several brown colors, it can be seen that the brightness is decreasing and the chromaticity values increase significantly.

For zone III we have almost a stable brightness values and a continuous decreasing for chromaticity values. In this region, because of the high value of the nitrogen content and a low brightness the films present a dark blue color.

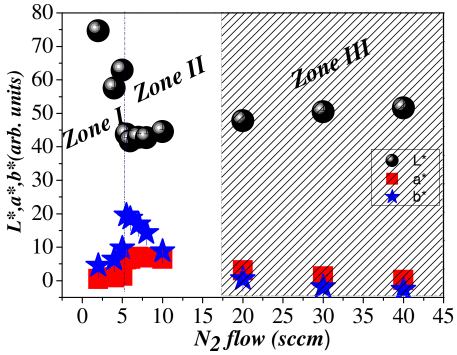

Fig. 5. *L^* coordinate and chromaticity coordinates (a^* and b^*) of the CIELAB 1976 colour space, under the standard CIE illuminant D65*

4. Conclusions

The experimental data presented above offers an image of the reactive sputter deposition of zirconium nitride. A systematic decrease in the deposition rate with the increase of the nitrogen fraction was observed, revealing the existence of three different sputtering modes.

The N_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 11 coatings presents different evolution, but the three regimes (Zone I, Zone II and Zone III) remains clearly defined even if we use different characterization techniques.

The colors of the films are changed from a metallic color in Zone I, to different brown colors in transition zone (Zone II) to the last zone where the films showed a dark blue color.

Zone I reveals the higher values of brightness and an increase of chromaticity values.

In Zone II it can be seen that the brightness (L^*) is decreasing and the chromaticity (a^*, b^*) values increase significantly. In zone III the brightness has almost a stable value and the chromaticity is still decreasing (negative b^* values and relatively low a^* values) at higher flow rates (>15 sccm).

During the characterization process of the films, has been observed that the aspects of coatings dependents on the chemical composition, and microstructure, which are closely correlated with the deposition technique and parameters.

These decorative films can be used in a various domains and applications like decorative coatings of plastic parts, bathroom appliances, car parts and components, or in high tech industry.

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