

## Influence of the O/C ratio in the behaviour of $\text{TiC}_x\text{O}_y$ thin films

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Available online 9 August 2006

### Abstract

The main purpose of this work consists in the preparation of single layered titanium oxycarbide,  $\text{TiC}_x\text{O}_y$ , thin films. The obtained results show that the evolution of the different elements concentration with the oxygen flow can be divided into 3 different regimes — i) carbide, zone I, ii) transition, zone T, and iii) an oxide one, zone II. Structure characterization results showed that the films crystallize in a TiC B1–NaCl-type crystal structure in the carbide regime. The films within the transition zone show a progressive tendency for amorphization, with the co-existence of a mixture of both poorly crystallized fcc TiC and TiO phases. For the highest oxygen flows, the films are practically amorphous. A broad range of colours was obtained from golden to metallic with different brilliances. An increase in hardness within the carbide zone was observed with increasing oxygen flow up to 1.5 sccm, and then followed by a systematic decrease with increasing oxygen flows.

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PACS: 68.55.Jk; 68.55.Ln; 68.55.Nq; 68.60.Bs; 78.20.Ci; 78.66.Sq; 81.15.Aa; 81.15.Cd

Keywords: X-ray diffraction; Phase transitions; Decorative films; Hardness

### 1. Introduction

The fourth-column transition metal nitrides have interesting properties resulting from the combination of both metallic and covalent bonding characteristics. Covalent material properties such as high melting points, high hardness and good thermal and chemical stability, are among the most appreciated ones. Regarding the metallic characteristics, electrical conductivity and metallic reflectance are two of the most important ones. Finally, the gold like appearance of some of these nitrides (e.g. TiN and ZrN), resulting from the high reflectance of these materials at the red-end of the visible spectrum, with low reflectance near the ultraviolet region [1], is a characteristic that make these materials very suitable and searched for decorative purposes. In fact, in the last few years this decorative thin film technology is gaining more and more importance that can be evaluated by the number of recent publications in the field and/or once combine the fundamental knowledge in the thin films with the industrial needs [2].

Regarding the apparent colorations of thin films, one must distinguish between the inherent colorations (e.g. in nitrides, carbonitrides or borides) and apparent colorations due to interference effects (e.g. transparent oxide or ultra-thin absorbing films). Since the apparent colorations of interference films are primarily influenced by thickness [3], their use appears to be less suitable choices as decorative coatings than the formers. The increasing demands for low cost products and reduced material resources imply that the continuous change in target material to obtain different coloured films is clearly non-suitable.

Recently, a new class of materials is gaining importance for decorative applications, the so-called metallic oxynitrides,  $\text{MeN}_x\text{O}_y$  (Me=early transition metal) and metallic oxycarbides,  $\text{MeC}_x\text{O}_y$  [4–12]. This importance results from the fact that the presence of oxygen allows the tailoring of film properties between those of “pure” metal nitrides/carbides and those of the correspondent oxides. Tuning the oxide/nitride (carbide) ratio allows one to tune the band-gap, bandwidth, and crystallographic order between oxide and nitride/carbide and hence the electronic properties of materials and thus the optical ones, including colour.

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The available research works suggest that the performance of these oxynitrides/oxycarbides depends not only on the deposition method but also on both the concentration and distribution of the oxygen atoms incorporated into the matrix [4–15]. Taking this into consideration, the main purpose of this work consists on the preparation and characterization of coloured films, based on single layered metal oxycarbides,  $\text{MeC}_x\text{O}_y$  ( $\text{Me}=\text{Ti}$ ).

## 2. Experimental

The  $\text{TiC}_x\text{O}_y$  films were deposited by reactive dc magnetron sputtering, from Ti and C targets (99.6% purity and with  $200 \times 100 \text{ mm}^2$  of size each), onto polished high-speed steel (AISI M2), single crystalline silicon wafers with (100) orientation, and stainless steel (AISI 316) substrates. The substrates were ultrasonically cleaned and sputter etched for 15 min in an Ar atmosphere (pressure of 0.15 Pa). The depositions were carried out in a laboratory-size deposition system, consisting of two vertically opposed rectangular magnetrons (unbalanced of type 2), in a closed field configuration. The films were prepared with the substrate holder positioned at 70 mm in all runs, using dc densities ranging from 12.5 to  $100 \text{ A m}^{-2}$  on the Ti target and  $25 \text{ A m}^{-2}$  in the C target. A gas atmosphere composed of Ar and O was used. The Ar flow was kept constant at 60 sccm and the oxygen gas flow varied from 0 to 10.5 sccm. The working pressure was approximately constant at 0.4 Pa and the substrates were biased at  $-70 \text{ V}$ . A Ti adhesion layer ( $\sim 0.30 \mu\text{m}$ ) was used in all films.

The atomic composition of the as-deposited samples was measured by Rutherford Backscattering Spectroscopy (RBS) using a 2 MeV  $\text{He}^+$  beam as well as 1.4 and 2 MeV proton beams to increase the accuracy in the O and C signals. Ball crater tests were used to measure the thickness of the samples. The crystallographic structure was investigated by X-ray diffraction (XRD) in the Bragg–Brentano configuration, using monochromatic Cu  $\text{K}\alpha$  radiation. The characterization of the film's colour was computed using a commercial MINOLTA CM-2600d portable spectrophotometer (wavelength range: 400–700 nm), using diffused illumination at an  $8^\circ$  viewing angle. The spectrophotometer was equipped with a 52 mm diameter integrating sphere and 3 pulsed xenon lamps. Colour specification was computed under the standard CIE illuminant D65 (specular component excluded) and represented in the CIELAB 1976 colour space [16,17]. Film's hardness and Young's modulus were determined from the loading and unloading curves, carried out with an ultra low load-depth sensing Berkovich nanoindenter from CSM Instruments. Residual stresses,  $\sigma_r$ , were obtained from the substrates curvature, using Stoney's equation [18].

## 3. Results

The film thicknesses ranged from 0.6 to  $1.9 \mu\text{m}$ . Carbon and oxygen contents (normalized to the titanium content) will be noted in the text as  $x$  and  $y$ , respectively. The variation of the film's Ti, C and O concentrations, obtained by RBS using the

RUMP code simulations [19] is plotted in Fig. 1 as a function of the O gas flow. The plot shows that the O content increases linearly with the increasing of the O flow rate, and the Ti content decreases as O flow rate increases. The C content is almost constant ( $\approx 20 \text{ at.}\%$ ) in all the oxycarbides depositions, with the exception of high O flows.

A closer look at the plot of Fig. 1 shows that the evolution of the different elements concentration with the O flow can be divided into 3 different regimes — i) carbide — zone I, ii) transition — zone T and iii) an oxide one — zone II. These distinct zones are, as it will be shown later in this paper, directly correlated with the structural features of the films. The first regime — carbide one, includes the group of samples prepared with O flows of 0.5, 1.0 and 1.5 sccm, with an atomic ratio of the elements,  $(\text{C}+\text{O})/\text{Ti}$ , up to one (Fig. 1). The first film (prepared with 0.5 sccm of O) is the characteristic of substoichiometric titanium carbide films,  $\text{TiC}_x$ . Up to this value of O flows (1.5 sccm), the main factor that might account for the observed behaviour is that the target is not or only slightly oxidized. As a result of the corresponding so-called elemental sputtering mode (ESM), similar to that already observed for pure metal targets [20,21], O enrichment increases linearly with increasing O flow rate (see Fig. 1).

No significant changes in the C target potential were observed ( $V \sim 700 \text{ V}$ ), while in the Ti one this target potential varied from 370 V at 1.5 sccm to 448 V at 2.5 sccm and 490 V at 3 sccm O flows. These results show a significant and increasing poisoning of the Ti target, and no significant changes in the C target. Nevertheless, the reduction of the C content from the film prepared without O from  $\sim 35 \text{ at.}\%$  down to  $\sim 20 \text{ at.}\%$  in the oxycarbide films induces that, although not much, there must be also some degree of target poisoning in the C target. A titanium oxide layer is progressively formed at the surface of the Ti target. As previously mentioned, the  $\text{C}+\text{O}$  content ( $x+y$ ) grows to about 1 for the depositions within the carbide regime, increasing from 1 to about 2 in the transition zone, and to values higher than 2 for films deposited at highest reactive gas flows (oxide regime).

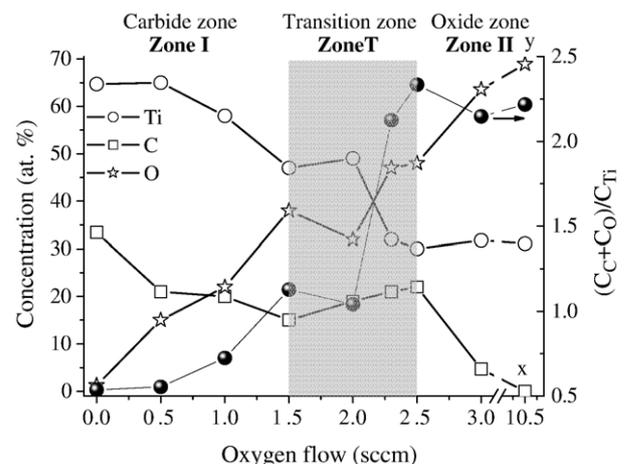


Fig. 1. Variation of the concentration of titanium, carbon and oxygen (open symbols) and the ratio  $(\text{C}+\text{O})/\text{C}_{\text{Ti}}$  (solid circles) as a function of oxygen flow rate.

The above-mentioned growth regimes changes can also be evidenced in the structural features revealed by the XRD results, shown in Fig. 2. The figure shows the XRD patterns for samples prepared within the different sputtering regimes, where the structural differences within each zone are evidenced. For comparison purposes, the result from a pure oxide sample ( $\text{TiO}_{2.2}$ ) is also shown. For the carbide regime, the films crystallize in a TiC B1–NaCl-type crystal structure (ICDD card No. 32-1383). In fact, TiC has a typical face centered cubic (FCC) structure with a lattice parameter  $a_0=0.43274$  nm (ICDD card No. 32-1383). Regarding the behaviour observed in each of the different growth zones, the results show that the TiC phase is the only one clearly observed in the carbide zone, with some tendency for an increase in the peak intensity ratio  $I_{(200)}/(I_{(111)}+I_{(200)})$  with the increase in the O flow, indicating a preferential crystalline growth change.

In this carbide zone, there are no clear traces of oxide phases in the diffractograms, which may exist in the amorphous form. The existence of some O inclusions within the TiC lattice (a significant number of vacancies may exist due to the low C contents), is also a factor that must be taken into account. Indeed, it is known that TiC is isomorphous with TiO [22].

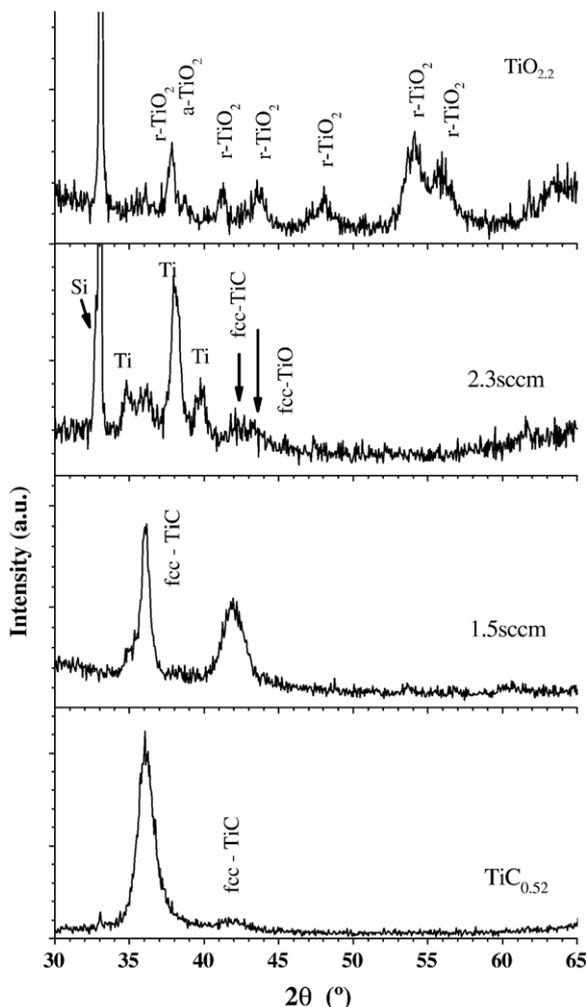


Fig. 2. XRD patterns for selected  $\text{TiC}_x\text{O}_y$  films. A  $\text{TiC}_x$  and a  $\text{TiO}_y$  films are shown for comparison purposes.

Thus, O as an impurity may substitute C to form binary solid solutions over a wide range of homogeneity [22]. Due to the very high chemical affinity of Ti to O, this element may be incorporated into the TiC films during growth [23–25].

Regarding the films within the transition zone (O flows between 1.5 and 2.5 sccm), the main result from the diffractograms (illustrated by the sample prepared with 2.3 sccm of O) was the progressive tendency for the amorphization of the films, with the co-existence of a mixture of both poorly crystallized fcc TiC and TiO phases. The fact that TiC is isomorphous with TiO [22] is consistent with this result. Nevertheless, as the O flow increases, this phase mixture becomes very difficult to be detected and the film prepared at 2.5 sccm is almost amorphous. The diffraction peaks from the adhesion layer are the only ones that are detected. In this transition zone, the amount of available O is already significant (roughly between 35 and 45 at.% in comparison with the Ti concentration which varies between 50 and ~35 at.%) and thus the formation of oxides is favoured. The insertion of O atoms in the TiC lattice can also occur and might explain the almost amorphous nature of the existing TiC grains (see the very broad peaks corresponding to (111) and (200) planes of the 2.3 sccm sample in Fig. 2), but due to the high concentration of O atoms, there is an increasing probability of having other O atoms as nearest neighbours, and thus favouring the formation of oxide phases, beyond that oxygen-doped carbide phase formation. This can also explain the decrease of the residual stress states as shown in Fig. 3. For the highest O flows ( $>2.5$  sccm), the films tend to be practically amorphous with no clear evidences of both TiC and oxide phases. The  $\text{TiO}_2$  sample (prepared with an O flow of 10.5 sccm and with a composition very close to the stoichiometry Ti:O — 1:2) shows a mixture of both anatase and rutile phases, while no such traces are clearly evidenced in that 3 sccm Ti–C–O sample.

Fig. 3 shows also the change in film hardness and Young's modulus as a function of the O flow. The first noticeable result is the increase in hardness within the carbide zone with increasing O flow. This increase has its maximum in the sample prepared at 1.5 sccm, and is then followed by a systematic decrease with increasing O flows, both in the transition and oxide zones, showing that again O is playing a fundamental role.

When using ternary nitrides, based on the introduction of an element in a well-known binary nitride, such as here adding O to TiC, the concentration of the added element is seen as a major parameter with a significant role for the observed behaviour. The first increase observed in the carbide region might be the result of the O doping of the TiC lattice, giving rise to a solid solution hardening mechanism. With O insertion, an increased strength of the material due to lattice distortions is expected [26]. The distortion inhibits the mobility of the dislocations, thus inducing an enhancement in hardness. When going from films prepared within the transition and oxide regimes, the oxide phase starts to develop and the hardness tends to be reduced, where the rule of mixtures is probably the main parameter that explains this behaviour. Beyond these structural features, the residual stresses seem also to be an important factor to account for this variation. In fact, the stress reduction

observed in Fig. 3 with increasing O flow is consistent with hardness reduction, but the structural changes that occur are also playing a decisive role. For instance, the sample prepared with 1.5 sccm has very low stresses, but has the highest hardness.

All these distinct behaviours occurring within the different zones can also be correlated with the film's colour characterization (Fig. 4). This figure shows the colour coordinates  $L^*$ ,  $a^*$  and  $b^*$ , represented in the CIELAB (1976) colour space [16,17]. As can be seen from the figure, with increasing flow rate from 0.5 to 1.5 sccm (including the  $\text{TiC}_{0.52}$  sample), the value of  $a^*$  (redness) increases as well as the  $b^*$  value (yellowness), which in fact reaches its maximum value. The  $L^*$  values (brilliance) show a slight decrease for the Ti–C–O films with the increase of O flow rate. The colour changes from metallic tone for the 0.5 sccm film (also for the  $\text{TiC}_{0.52}$  film) to a very bright yellow-pale at 1 sccm and to a golden tone for the 1.5 sccm film. With further increase of the O flow rate (transition zone), the film colour changes to red-brownish (presenting the highest values of  $a^*$ ) for films prepared with 2.0 and 2.1 sccm and to dark grey tones (low positive  $a^*$  and  $b^*$  values) for films prepared with 2.3 and 2.5 sccm. A significant decrease of  $L^*$  values were obtained for films deposited within this transition zone. For O flows higher than 2.5 sccm the films have a very dark grey tone, tending to the development of interference colour (rainbow-like appearance). The  $L^*$  coordinate becomes almost constant at a value of about 45. These results indicate a strong influence of the O flow on film colour, which is related with the structural changes previously discussed. In fact, the different growth zones showed to develop different structural features, which in its turn showed to be consistent with the optical characteristics of the films.

In the transition zone, a significant reduction of  $L^*$  and  $b^*$  was observed (with  $a^*$  showing the highest values followed by a significant reduction) that can be explained by the decreasing metallic character of the films and the transition towards a more insulating type represented by the oxide-type films prepared at the highest O flows. The electron charge transfer from Ti atoms to O and C atoms increases with increasing C+O content in Ti–C–O. Higher O+C contents result in higher consumption of free  $d$  electrons from Ti atoms and less free  $d$  electrons are

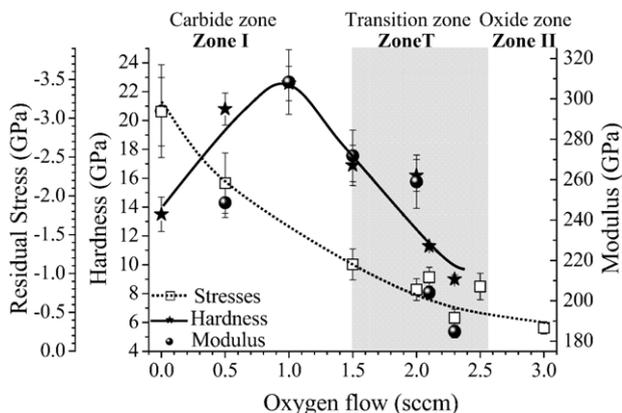


Fig. 3. Film residual stresses, hardness and Young's modulus evolution of sputtered  $\text{TiC}_x\text{O}_y$  films as a function of the oxygen gas flow.

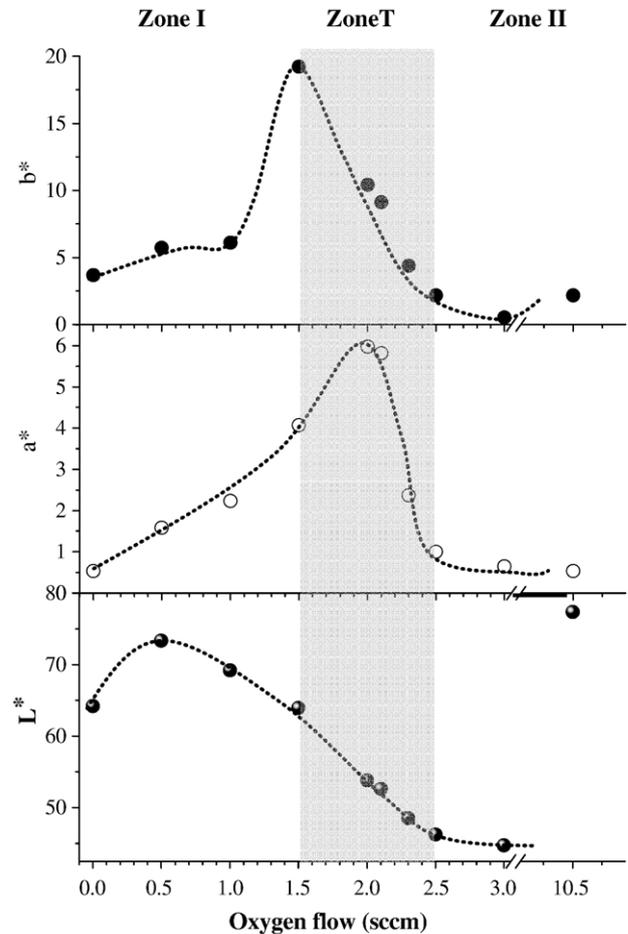


Fig. 4. Average colour coordinates in the CIELAB 1976 colour space under the standard CIE illuminant  $D_{65}$ , for films prepared with different oxygen gas flows.

available for conductivity. Consequently, brilliance ( $L^*$ ) drops with increasing O+C amounts.

#### 4. Conclusions

Thin Ti–C–O films were prepared by dc reactive magnetron sputtering from high purity Ti and C targets. The obtained results show that the evolution of the different film's properties can be divided into 3 different regimes — i) a carbide one (O flows from 0.5 to 1.5 sccm), ii) a transition zone (including the films prepared with O flow from 1.5 and 2.5 sccm) and iii) an oxide one (which includes the films prepared with O flow higher than 2.5 sccm). These different regimes were directly correlated with the composition and structural changes occurring in the films.

The films prepared within the carbide regime crystallize in a  $\text{TiC B1-NaCl}$ -type crystal structure, while in the transition zone a progressive tendency for the amorphization is observed, with the co-existence of a mixture of both poorly crystallized TiC and TiO phases. For the highest O flows, the films tend to be practically amorphous.

Colour changes from metallic tone for the 0.5 sccm film to a very bright yellow-pale at 1 sccm and to a golden tone for the 1.5 sccm film. With further increase of the flow rate (transition zone), the colour changes to red-brownish for films prepared

with 2.0 and 2.1 sccm and to dark grey tones for films prepared with 2.3 and 2.5 sccm. For O flows higher than 2.5 sccm the films have a very dark grey tone, tending to the development of interference colours (rainbow-like appearance). These results indicate a strong influence of O on colour, which is directly related with the structural changes. In the transition zone, a significant reduction of  $L^*$  and  $b^*$  was observed (with  $a^*$  showing the highest values followed by a significant reduction) that can be explained by the decreasing of the metallic character of the films and the transition towards a more insulating type, represented by the oxide-type films prepared at the highest O flows.

An increase in hardness within the carbide zone was observed with increasing O flow. This increase has its maximum for the sample prepared with 1.5 sccm, followed by a systematic decrease with increasing O flow, both in transition and oxide zones.

### Acknowledgments

The authors gratefully acknowledge the financial support of the Portuguese FCT institution by the project n° POCTI/38086/CTM/2001 co-financed by European community fund FEDER.

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