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Development of dark Ti(C,O,N) coatings prepared by reactive sputtering

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Direct current reactive magnetron sputtering was implemented to successfully deposit dark Ti(C,O,N) thin films on silicon substrates. A titanium target was sputtered while a mixture of oxygen and nitrogen was injected into the deposition chamber, independently from an acetylene source. The deposition parameters were chosen as a function of pre-existing knowledge about sputtered Ti-O-N and Ti-C-O films. Tuning the oxygen / (nitrogen + carbon) ratio allowed obtaining a large spectrum of properties. In particular, the colour of the films was characterized by spectral reflectance spectroscopy, and expressed in the CIE 1976 L*a*b* colour space. An accurate control of the reactive gas mixture flow rate allowed obtaining intrinsic, stable and attractive dark colour for decorative applications. Surprisingly, the coatings with the lowest content of carbon and the highest content of oxygen presented the darkest tones.

Composition analysis by electron probe microanalysis was done to quantify the titanium and metalloid concentrations in the films. X-ray diffraction experiments revealed the evolution of the film structure from an fcc structure for the lowest ($O_2 + N_2$) flow rates to an amorphous one for the highest flow rates.

1. Introduction

Decorative thin films have been used for a long time, to golden metallic parts with titanium nitride [1] or for blackening metal objects in cars with carbon layers, for instance. Today, decorative coatings are increasing their commercial importance, especially concerning high-quality products like eyeglass frames, wristwatch casings, wristbands or pens. Together with attractive colours, decorative coatings must provide high wear resistance, surface quality, skin compatibility and protection against corrosion.

A wide range of colours can be reached now, some are intrinsic and others are obtained by interference. Transition metal oxynitride thin films (titanium, zirconium …) are used to get brown, golden, green, purplish-pink, blue, or violet tones. Some black coatings have been obtained as Cu-Ni films deposited by electrochemical deposition [2], Ni-P alloys by electroless plating [3], and Ti-N-(C,Al) [4] or amorphous carbon coatings by sputtering [5]. But none of these studies presents more than one black tone.

This paper deals with the deposition of Ti-C-O-N decorative coatings by reactive magnetron sputtering. The goal is to produce coatings with several tones of black using the same chamber configuration and a minimum of materials, namely one target and two reactive gases, allowing economy of time and materials. Few publications were done on this quaternary system [6-8] and, as far as it is known, none of them focuses on the colours of these titanium oxycarbonitrides. A simple process using only two reactive gases, a pure gas and a gas mixture, was used to obtain very dark attractive colours. The colorimetric measurements were correlated to the atomic composition and the crystallographic structure.

2. Experimental details

The depositions of titanium oxycarbonitride thin films were performed in a laboratory-size unbalanced (type II) direct current (DC) magnetron sputtering system. The films were prepared with the substrate holder positioned at 70 mm from the target in all runs, applying a discharge current density of 100 $A.m^{-2}$ on the titanium target. The substrates (silicon wafers with (100) orientation and mechanically polished high speed steel AISI M2) were grounded and kept at a constant temperature T = 473 K during the one hour deposition, using an external heating resistance. The titanium target (99.96 % - 20×10 cm^2) was sputtered in an argon (working gas) + gas mixture (oxygen and nitrogen source) + acetylene (carbon source) atmosphere. The gas mixture was composed of nitrogen and oxygen, with a constant N_2:O_2 ratio of 17:3. The Ar flow and the acetylene flow were kept constant at 60 sccm and 5 sccm, which correspond to partial pressures of 0.47 Pa and 0.25 Pa, respectively. The gas mixture partial pressure, p_{O2+N2}, was systematically changed from 0 to 0.4 Pa by controlling the gas mixture flow rate (from 0 to 18 sccm). The base pressure was below 10^{-3} Pa.

The thickness of the coatings was measured with a CSM Calotest 01-211 device, by ball cratering. The elemental composition of the coatings was investigated with a Cameca SX-50 Electron Probe Micro Analysis (EPMA), operating at 15 keV as acceleration voltage. To note is that hydrogen could not be detected by EPMA. X-ray diffraction (XRD) experiments were performed in a Siemens D-500 apparatus using a Co Kα radiation (λ = 0.178897 nm) in Bragg-Brentano configuration. The film's colour was represented in the CIELab 1976 colour space by using a commercial Minolta CM-2600d portable spectrophotometer (wavelength range: 400-700 nm), with diffused illumination (D65 light source) at an 8º viewing angle (specular component included). It was equipped with a 52 mm diameter integrating sphere and 3 pulsed xenon lamps. The observer was placed at a 10º angle. The reflectance was measured by UV-visible spectroscopy in the 200-900 nm range using a Varian Cary 500 spectrophotometer.

3. Results and discussion

3.1 Target potential and deposition rate

As commonly observed during reactive sputtering experiments, the variation of the oxygen and nitrogen mixture partial pressure strongly affects the titanium target voltage (Fig. 1). The evolution of the target potential shows that two different regimes are present. In the first part of the plot, the decrease in target voltage, measured for films prepared with very low partial pressures (below 0.11 Pa), can be attributed to the evolution of the composition of the target surface and thus to the change of the ion induced secondary electron emission coefficient (ISEE) at the surface. Since the ISEE is usually much higher for compounds than for metals, and especially for oxides [9], a decrease of the plasma impedance is expected. Then, since the current density applied to the Ti target is constant, a decrease of the target voltage is expected.

For $p_{O2+N2} > 0.11$ Pa, the abrupt target voltage increase may be attributed to the presence of non-reacted oxygen/nitrogen (and even carbon) on the target surface. When the reactive gas mixture partial pressure increases above this critical value, the target oxidation (poisoning effect) starts to prevail (resulting from the increased ionization of these reactive gases, which evolves to their actual dissociation) and hence a contamination layer (oxide/nitride) grows on the target surface. The increase of the contamination layer thickness on the target surface decreases the electrical conductivity of the target. Therefore a higher cathode potential is necessary to break this insulating barrier on the target. This induces an increase of the cathode potential from ~470 to 537 V with the increase of gas mixture partial pressure from 0.11 to 0.3 Pa.

In accordance with the target voltage evolution, the deposition rate, R_d, displays two similar zones. Without injection of the gas mixture (only argon and acetylene), the deposition rate is the highest, around 2.1 μm h^{-1}. When the reactive gas mixture (O_2+N_2) partial pressure increases, R_d decreases and stabilizes around 1 μm h^{-1} for p_{O2+N2} higher than 0.18 Pa. For the highest partial pressures, which correspond to the poisoned target regime, the injection of gas mixture is now high enough to fully run the process in the oxide(nitride)-type sputtering mode. The sputtering yield of the poisoned target (titanium oxide(nitride)) is much lower than that of titanium [10-11], and thus the deposition rate largely decreases, as shown in Fig. 1.

3.2 Atomic composition

Elemental composition measurements carried out by EPMA on Ti(C,O,N) samples show a global opposite evolution of titanium and carbon contents from one side and oxygen and nitrogen in the other side, when the (O_2+N_2) partial pressure increases (Fig. 2). The stoichiometry varies from $TiC_{0.65}O_{0.15}$ to $TiC_{0.77}O_{1.20}N_{1.37}$, for ($O_2$+$N_2$) partial pressures of 0 and 0.4 Pa, respectively. The results are consistent with the increase of the gas mixture flow rate. From Fig. 2, the first conclusion to be drawn is that there is a regular increase of the oxygen content with increasing the gas mixture partial pressure. On the other hand, the nitrogen content increases up to approximately 30 at. % ($p_{O2+N2} = 0.11$ Pa) and stays approximately constant for $p_{O2+N2} \geq 0.11$ Pa. The value $p_{O2+N2} = 0.11$ Pa seems to be the limit between two zones that can be defined in this figure, corresponding, in fact, to the same limit observed in Fig. 1 for the evolution of both the deposition rate and the target potential. This shows a good correlation between the two sputtering modes and the composition of the films. In the $0 < p_{O2+N2} < 0.11$ Pa range, the titanium content decreases abruptly from 55 to 27 at. % and the carbon content decreases from 36 to 28 at. %. In the same range, the oxygen content rises from 8 to 15 at. % and the nitrogen from 0 to 28 at. %. This must be correlated to previous results on titanium oxynitrides for which a similar reverse evolution of titanium and oxygen (or nitrogen) by simple variation of the oxygen supply, was observed [12-13]. For the low flow rates, the films are varying between sub-stoichiometric and nearly stoichiometric conditions and thus most of the sputtered atoms as well as the reactive ones present in the plasma are adsorbed in the growing film. In this part, the evolution of the film composition strongly depends on the gas mixture partial pressure. It should be noticed that the standard enthalpies of formation of TiC, TiN, TiO and TiO_2 compounds are respectively, -184 kJ.mol^{-1}, -338 kJ.mol^{-1}, -520 kJ.mol^{-1} and -942 kJ.mol^{-1}. This higher affinity of titanium towards oxygen induces much higher oxygen content in the film (Fig. 2) than the one expected from the gas mixture.

For $p_{O2+N2} > 0.11$ Pa, the titanium and nitrogen contents are constant around 20 at. % and 32 at. %, respectively, while oxygen continuously increases from 15 to 28 at. % (much higher than the 17:3 ratio in the gaseous phase). The carbon content presents a decrease down to 18 at. % for $p_{O2+N2}= 0.4$ Pa. The film composition changes slowly with the mixture partial pressure.

3.3 Crystallographic structure

The structural evolution of the Ti(C,O,N) coatings as a function of the gas mixture partial pressure is shown in Fig. 3. X-ray diffraction patterns of the films deposited on (100) silicon substrates reveal a strong dependence of the film texture on the gas mixture partial pressure, as well as the atomic composition. For the titanium carbide film (0 sccm for the gas mixture flow or $p_{O2+N2} = 0$ Pa), diffraction peaks corresponding to the fcc TiC phase appear with a preferential orientation along the (111) direction, but (200) and (220) diffraction peaks are also observed with quite a lower intensity. The crystallite size calculated by the Scherrer’s method from the full width at half maximum of the (111) diffraction peak is 16 nm. When the O_2+N_2 gas mixture is injected, the (111) preferential orientation disappears as previously reported for other Ti(C,O,N) coatings [8]. For low partial pressures (0.09 and 0.11 Pa), the films exhibit peaks shifted to higher angles, corresponding to an fcc structure, which may be a titanium carbide structure with inclusion of oxygen and/or nitrogen atoms ($TiC_x(O,N)$). It is important to note that TiC, TiN and TiO present the same crystallographic structure with close lattice parameters (a_{TiC} = 0.4328 nm from JCPDS04-004-2919, a_{TiN} = 0.4241 nm, JCPDS04-001-2272 and a_{TiO} = 0.4177 nm, JCPDS04-001-6834). Therefore, X-ray diffraction is not a suitable method to distinguish between these three compounds (especially in a sub- or over-stoichiometric condition such as the one possible in this case), or a solid solution-type compound, where all or some of C, O and N atoms may be within the same cubic lattice. Anyway, XRD analyses clearly show that Ti(C,O,N) films deposited at low p_{O2+N2} exhibit an fcc structure. When p_{O2+N2} grows from 0.09 to 0.18 Pa, the three main peaks located around 42º, 49º and 73º become less intense and disappear for the highest gas mixture partial pressures (0.4 Pa): the films containing a strongly dominant metalloid concentration clearly exhibit an amorphous structure. These structural features show a clear coherency with the two zones illustrated in both figures 1 and 2. The crystalline films are those located in the first zone ($p_{O2+N2} < 0.11$ Pa), where the composition of the films is sub- to roughly stoichiometric (ratio of N+O+C over Ti roughly higher than 0.7). Moreover it is important to emphasize the slight decrease of the carbon content, for $p_{O2+N2} \leq 0.11$ Pa, which may be related with the lowest value of standard enthalpy of formation for TiC. The fact that the ratio N+O+C over Ti is increasing rapidly above 1 ($p_{O2+N2} > 0.11$ Pa) makes the films pass from a situation where almost all arriving species are added to the growing film (first zone), to a zone where the excess of N+O+C in respect to Ti is most likely inducing some preferential reactions of Ti, according to the reactivity of each reactive gas. In the second zone, the films lose their long range order, which may result from the joined effects of both low surface diffusion of the particles impinging on the substrate or the growing film (the depositions were made at only

473 K), and the significant over-stoechiometric condition of the films (Ti is only around 20 at. % within the higher partial pressures zone).

Although the available thermodynamic data of all binary compounds may induce some tendency to form preferentially an oxide-based compound (TiO_2-based), Fig. 2 shows that the ratio of O over Ti roughly varies between 0.5 and 1.2 and thus this tendency might be somehow reduced. Moreover, the ratio of N over Ti is around 1.5 throughout this high pressures zone. These ratios certainly impose a great deal of difficulties within the structural arrangements. One possibility is that the former cubic lattice becomes significantly Ti deficient with many (N, O, or even C) interstitials/substitutions which induce significant lattice distortions. Another possibility is that a nano-scaled type composite may be present, where nano-grains (cubic lattice type, with Ti vacancies and mixed O+N) are dispersed in a C amorphous phase. Anyway, this amorphisation was already observed for high contents of oxygen in ternary compounds like Ti(O,N) [14-15] or Ti(C,O) [16] sputter deposited thin films.

3.4 Decorative properties

Colour specification of the films deposited on silicon is represented in the CIELab colour space in Fig. 4. It can be noticed in this figure that the gas mixture partial pressure of 0.11 Pa is again the limit between two groups of films. For $p_{O2+N2} < 0.11$ Pa, the brightness L* is higher than 56 %. Moreover, the b* value is higher than three, which makes the film tend to be dark grey and very slightly brownish. Then, for $p_{O2+N2} \geq 0.11$ Pa the brightness becomes lower than 50 and {a*;b*} tends to be closer to {0;0}. These samples are considered as black for a human observer. Actually the farther away a point from the centre {a*;b*}={0;0}, the higher the colour saturation. This quantity can be measured using the chromaticity $\sqrt{a*^2 + b*^2}$, expressing the amount of colour. In our case, the Ti-C film presents a chromaticity of 6.34 while the Ti(C,O,N) film deposited with p_{O2+N2} = 0.4 Pa has the lower chromaticity (1.87). This decrease can be divided in two steps. The chromaticity is higher than 2.5 for $p_{O2+N2} < 0.11$ Pa, and then is located between 2.5 and 1 for $p_{O2+N2} \geq 0.11$ Pa. Therefore the samples with the highest content of oxygen present the best colorimetric characteristics to be considered as black. It is important here to notice the advantage of the use of the gas mixture (oxygen and nitrogen). This mixture is used in order to obtain a smooth transition from the grey to the black, more easily than with a conventional process, by injecting nitrogen mixed with little oxygen, and increasing the window of possibilities to prepare coatings with low oxygen content.

This analysis is completed by the reflectance measurements in UV-visible range (Fig. 5). The films deposited with p_{O2+N2} = 0 and 0.09 Pa clearly present a similar behaviour. Their reflectance increases up to 28 and 35% at 900 nm, which can be correlated to a metallic behaviour. It is confirmed by the metallic aspect detected by eye. Except for p_{O2+N2} = 0.09 Pa, the film reflectance in the visible region decreases continuously when the p_{O2+N2} increases, indicating that the films become darker. The film deposited at p_{O2+N2} = 0.40 Pa exhibits an almost constant reflectance of 15 ± 2 % in the visible range.

The different reflectance behaviour and the metallic aspect of the films obtained with $p_{O2+N2} < 0.11$ Pa, with respect to those obtained for higher partial pressures can be related to the different structure of these films. For the higher partial pressures, the small variations of the colour parameters are in agreement with the slight variations of the composition of these X-ray amorphous films.

4. Conclusion

Together with argon (working gas) and acetylene (carbon source), a gas mixture with an appropriate N_2:O_2 ratio was used to deposit reactive sputtered Ti(C,O,N) coatings, varying the mixture flow rate. Structural characterisation results revealed a strong dependence of the structure on the oxygen + nitrogen partial pressure. Without injection of O_2+N_2, the films exhibited diffraction peaks corresponding to fcc TiC. For intermediate oxygen + nitrogen partial pressures, the diffraction patterns revealed an fcc (TiC, and/or TiO and/or TiN) phase. The films are amorphous for the highest partial pressures and thus oxygen contents. Finally, the metallic dark grey colour of titanium carbide became very dark or black with the increase of the oxygen content in the films.

The simple method used in this work to prepare the Ti(C,O,N) samples with different dark tones proved that one can smoothly tailor the decorative properties by adjusting only the flow rate of one gas mixture.

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Figure captions

Figure 1: Variation of the deposition rate of Ti(C,O,N) coatings and the target potential as a function of the (O_2 + N_2) partial pressure in the chamber.

Figure 2: Influence of the (O_2 + N_2) partial pressure on the atomic composition of titanium oxycarbonitride thin films (measured by EPMA).

Figure 3: X-ray diffraction patterns of titanium oxycarbonitrides deposited on silicon (100), with (O_2 + N_2) partial pressure p_{O2+N2} = a) 0 Pa; b) 0.09 Pa; c) 0.11 Pa; d) 0.15 Pa; e) 0.18 Pa. Vertical lines correspond to the TiC diffraction peak positions. The patterns were vertically shifted for the shake of clarity.

Figure 4: Average colour coordinates of Ti(C,O,N) films on silicon in the CIELab colour space under the standard CIE illuminant D_{65}, as a function of the (O_2 + N_2) partial pressure.

Figure 5: Reflectance spectra of titanium oxycarbonitride thin films on silicon substrates deposited with different (O_2 + N_2) partial pressures.

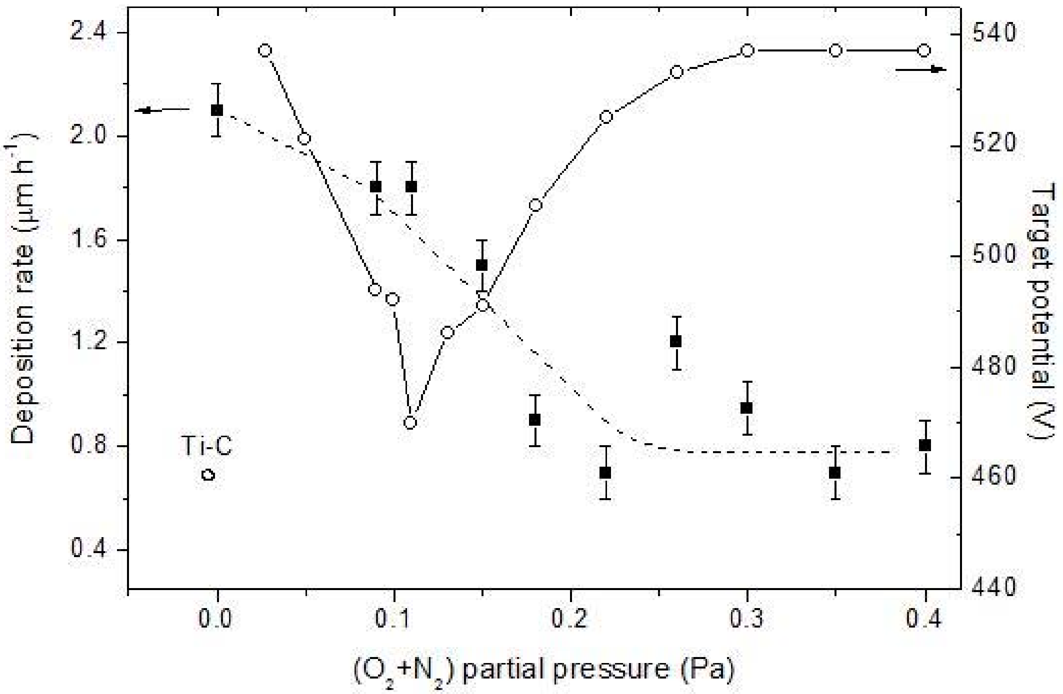
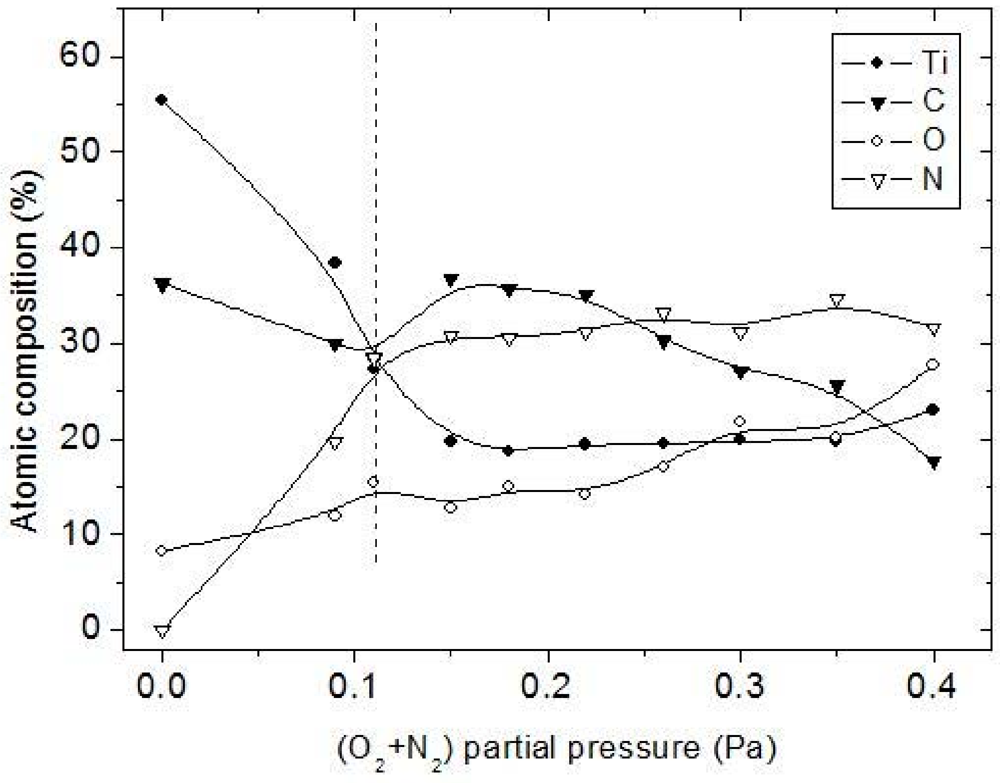

Deposition rate (μm h⁻¹)
Target potential (V)
(O₂+N₂) partial pressure (Pa)
Ti-C
2.4
2.0
1.6
1.2
0.8
0.4
540
520
500
480
460
440
0.0
0.1
0.2
0.3
0.4

Fig 1



Atomic composition (%)
0
10
20
30
40
50
60
0.0
0.1
0.2
0.3
0.4
(O_2+N_2) partial pressure (Pa)
Ti
C
O
N

Fig 2

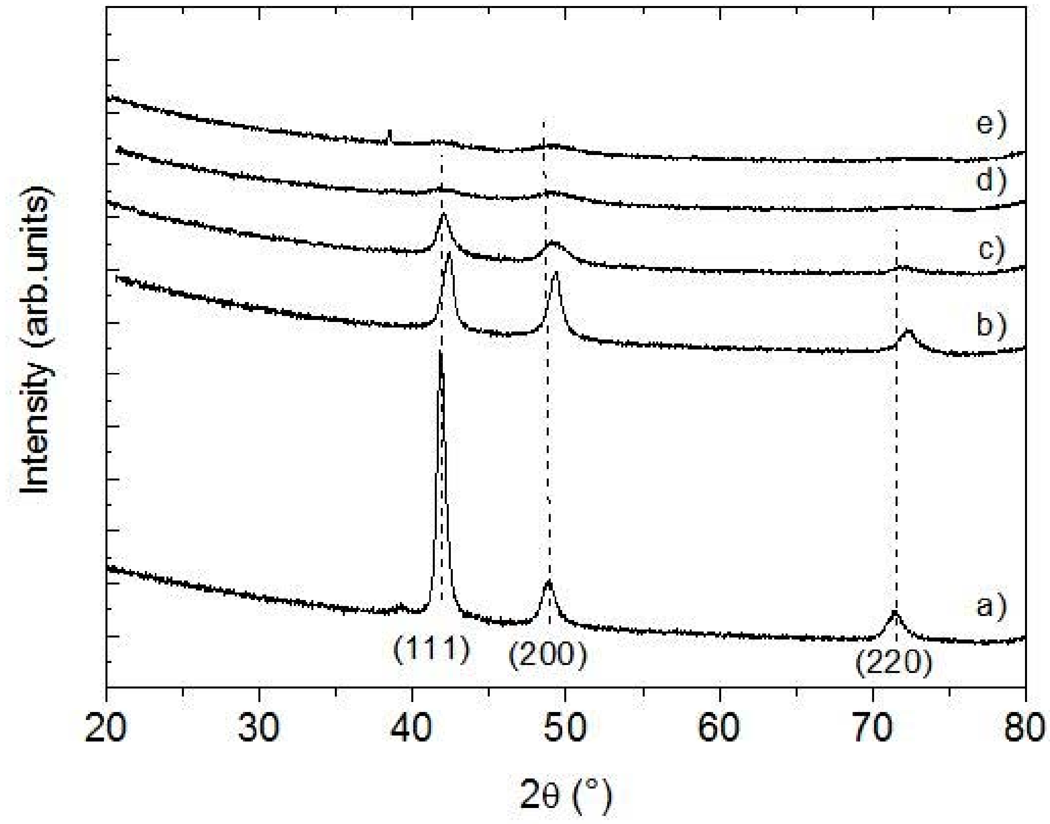


Fig 3

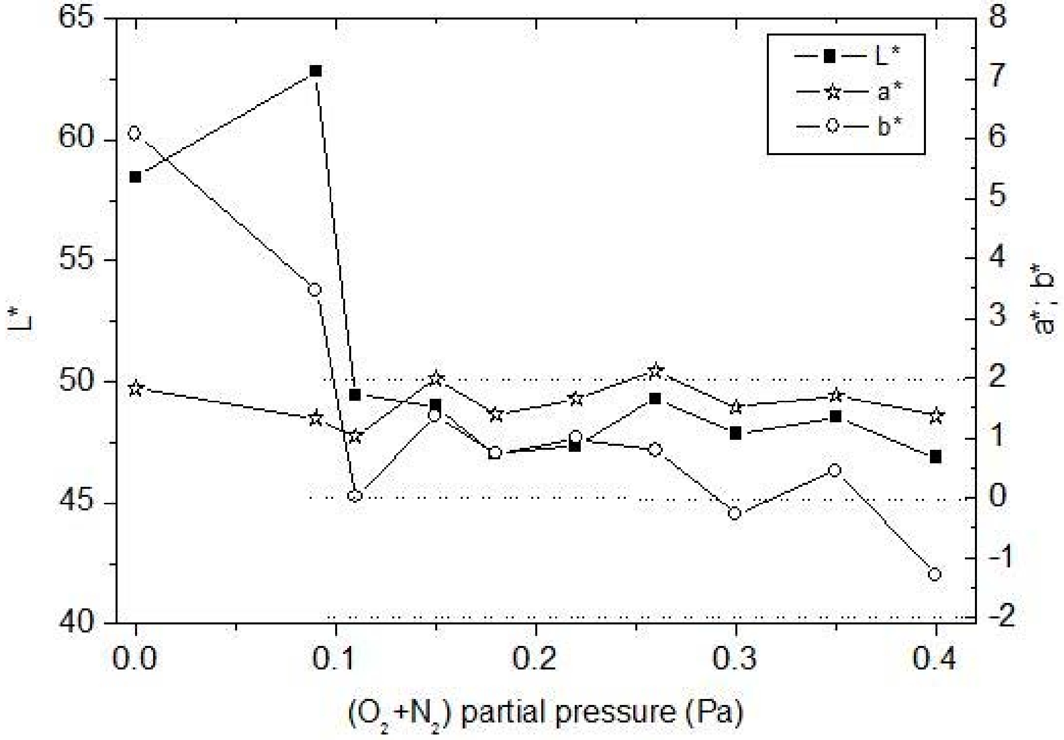

65
60
55
50
45
40
L*
8
7
6
5
4
3
2
1
0
-1
-2
a*; b*
0.0
0.1
0.2
0.3
0.4
(O2+N2) partial pressure (Pa)
L*
a*
b*

Fig 4

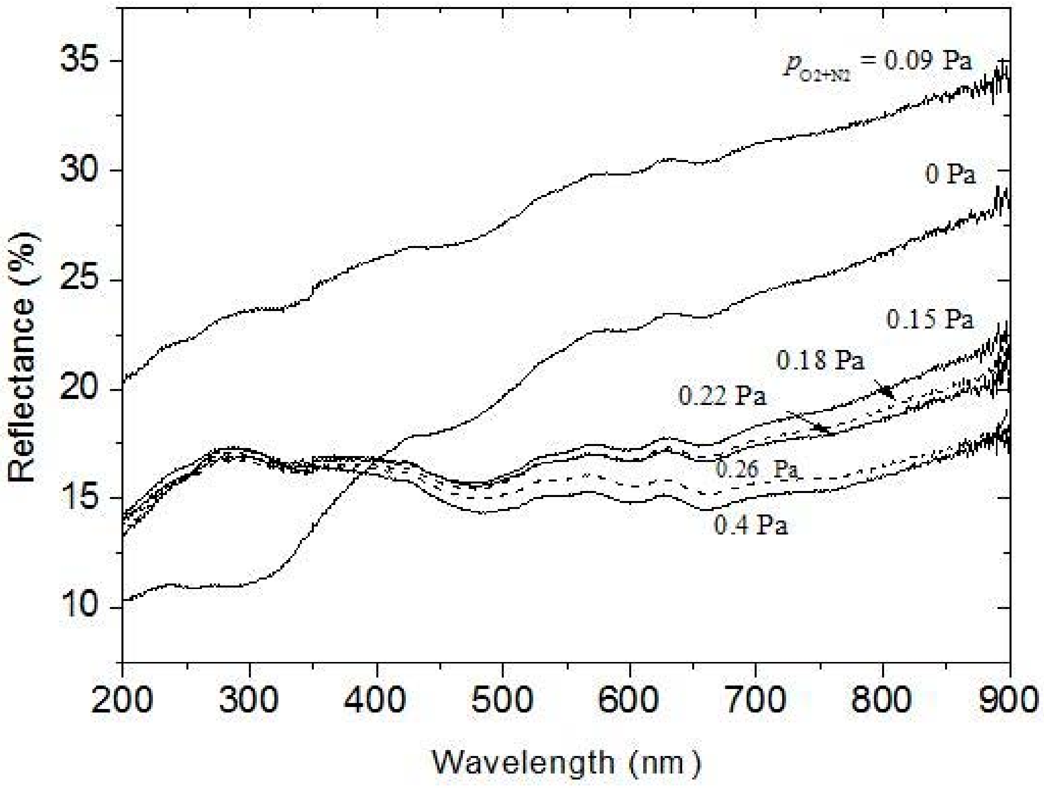

p_{O2+N2} = 0.09 Pa
0 Pa
0.15 Pa
0.18 Pa
0.22 Pa
0.26 Pa
0.4 Pa
Reflectance (%)
Wavelength (nm)
35
30
25
20
15
10
200
300
400
500
600
700
800
900

Fig 5