



Properties of CrN thin films deposited in plasma-activated ABS by reactive magnetron sputtering

Paulo Pedrosa^{a,b,*}, Marco S. Rodrigues^a, Miguel A. Neto^c, Filipe J. Oliveira^c, Rui F. Silva^c, Joel Borges^a, Margarida Amaral^d, António Ferreira^d, Luís H. Godinho^d, Sandra Carvalho^a, Filipe Vaz^a

^a Centro de Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

^b Institut FEMTO-ST, UMR 6174 CNRS, Université Bourgogne Franche-Comté, 15B Avenue des Montboucons, 25030 Besançon Cedex, France

^c Department of Materials and Ceramic Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

^d Prírev – Revestimentos Técnicos, Lda., Zona Industrial de Vagos – Lote 61, 3840-385 Vagos, Portugal

ARTICLE INFO

Keywords:

Sputtering
Chromium nitride
ABS
Metallization
Polymer coating

ABSTRACT

In this work, magnetron sputtered CrN_x thin films with nitrogen concentrations ranging from 17 to 30 at.% were deposited on plasma activated ABS. Two sets of thin films were obtained by varying the N₂ flow inside the vacuum chamber (series #1) and the deposition time (series #2). The polymer samples were also subjected to plasma treatment in Ar prior to the CrN_x thin films' deposition, in order to enhance the adhesion. The fundamental microstructural, chemical and physical properties, as well as the electrochemical and adhesion behavior of the CrN_x thin films, were assessed by SEM, XRD, 3D profilometry, RAMAN, colorimetry, OCP measurements and cross-cut tape test. Main results show that high-quality CrN_x films with a low percentage of defects were obtained. The CrN_x film sputtered with 3 sccm N₂ for 20 min was considered to possess the most appropriate brightness, color, electrochemical stability and interfacial adhesion to fit the end-user requirements. Magnetron sputtering is thus a promising alternative to the hazardous chrome plating for an effective metallization of ABS.

1. Introduction

Thin film-coated (metallized) polymers are replacing traditional metallic materials in many industrial fields, particularly in automotive [1], electronic [2], and wear protection applications [3]. The low density, flexibility, design versatility and low-cost production of most polymers [1, 4], combined with the properties of a shining, highly reflective and conductive metallic coating, gives them a considerable advantage over common metals [5].

Acrylonitrile Butadiene Styrene (ABS) is widely used in industrial applications such as automotive, electronic housings, computer and air conditioning parts [3]. This is due to its intrinsic properties, in particular, an outstanding impact resistance, good processability and dimensional stability, recyclability, and cost-effectiveness [1, 3, 5, 6]. As such, ABS dominates the market of metallized polymers [1].

One of the most common polymer metallization processes used in the last decades has been electroplating that produces environmentally dangerous waste products, such as the highly toxic hexavalent chromium used either in the surface activation/etching step [7] or in the chrome plating itself [5]. Hence, following all the enacted European

legislation during the last years against the use of hexavalent chromium solutions [8, 9], new chromium surface treatments [1] and plating alternatives have emerged and include chemical, physical, and mixed approaches [1, 3, 5].

Magnetron sputtering (MS) is one of such techniques [3, 10, 11], which can be used on a wide range of available polymers and has a reduced environmental impact, unlike chrome plating [12]. MS advantages and disadvantages over electroplating are effectively summarized in reference [13]. Electroless plating has the advantage of being capable of levelling the coated surface, which may lead to a superior decorative finishing and brightness, while the most attractive feature of MS may be the ability to coat most substrate materials with a wide range of thin film systems in an environmentally friendly and cost-effective way. Consequently, MS is becoming an increasingly attractive industrial process for polymer metallization, especially for the deposition of chromium nitride (CrN) films [14–18] for protective and decorative purposes [3, 11, 19]. Furthermore, MS allows for a simple and fine control of the process parameters (pressure, temperature, current, etc.) thus allowing an effective tailoring of the CrN thin film microstructures and properties obtained [19, 20], especially in polymers that

* Corresponding author at: Centro de Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal.
E-mail address: paulo.pedrosa@fisica.uminho.pt (P. Pedrosa).

Table 1
Plasma treatment and MS deposition process parameters.

Plasma treatment (before all depositions)				
Ar (Pa)	Power (W)		Time (s)	
80	100		300	
Series #1 (1.5 A, 25 sccm Ar, 20 min.)				
Sample #	U (V)	N ₂ (sccm)	N composition (at.%)	Thickness (nm)
1	284 ± 1	0	–	340 ± 50
2	308 ± 1	2	17.4 ± 5	370 ± 50
3	309 ± 1	3	16.8 ± 5	146 ± 50
4	305 ± 1	4	23.1 ± 5	230 ± 50
6	304 ± 1	6	29.2 ± 5	490 ± 50
8	303 ± 1	8	25.1 ± 5	230 ± 50
Series #2 (1.5 A, 25 sccm Ar, 3 sccm N ₂)				
Sample #	U (V)	t _{dep} (min.)	N composition (at.%)	Thickness (nm)
3	309 ± 1	20	16.8 ± 5	146 ± 50
9	307 ± 1	10	12.7 ± 5	119 ± 50
10	305 ± 1	30	23.1 ± 5	394 ± 50
11	304 ± 1	40	23.0 ± 5	661 ± 50
12	305 ± 1	60	23.1 ± 5	739 ± 50

are rather susceptible to high temperatures developed during the sputtering process [21]. Consequently, MS chrome metallization of ABS is an excellent alternative to electroplating since it allows the deposition of thin films with superior corrosion resistance, and mechanical and tribological properties [22–27].

In the present work, the authors aim at developing an environmentally friendly MS-based process for ABS chrome metallization that is able to deposit CrN films with protective and decorative properties comparable to the ones obtained traditionally by electroplating. As such, several end-user requirements such as the deposition of well-adhered, dense, defect-free, bright and reflective films with high chemical and electrochemical stability must be attained.

2. Experimental details

CrN thin films were fabricated by DC magnetron sputtering using a pure chromium target (200 × 100 × 6 mm³, 99.99% purity), in a custom-made 60 L vacuum chamber. All depositions were performed after a residual vacuum of approximately 10^{−4} Pa is attained inside the reactor. During the sputtering process, the gas atmosphere was composed of a mixture of Ar ($\phi = 25$ sccm, $p = 3.8 \times 10^{-1}$ Pa) and N₂ (0 ≤ ϕ ≤ 8 sccm, partial pressure varied 0.5 Pa). The plasma was ignited using a current density of 75 A·m². The grounded sample holder was used in rotation mode at 5 rpm in front of the target ($d_{\text{target-sample}} = 7$ cm). No external heating was used. The coated substrates were silicon (Boron-doped, p-type, <100> orientation, 525 μm thick) for chemical, morphological and (micro)structural characterization purposes, glass for the electrochemical behavior, ABS for color, brightness and reflectance measurements, and PET and PA for adhesion. Before all depositions, the surface of the substrates was subjected to a plasma treatment using a 40 kHz RF generator with a power of 100 W in an argon atmosphere (80 Pa for 5 min) for surface activation in a Low-Pressure Plasma Cleaner by Diener Electronic (Zepto Model). No sample bias was used in the pre-cleaning step. Further details regarding the plasma treatment and deposition process of both series of films are patent in Table 1.

The surfaces of the sputtered samples had to comply with several end-user requirements, hence the performed characterization was

specifically selected to target the desired thin film specifications. The morphological features were observed under a Hitachi SU70 Scanning Electron Microscope (SEM), equipped with a Bruker Energy Dispersion Spectroscopy (EDS) system used to assess the nitrogen incorporation in the films, and operated at 15 kV. The X-ray diffraction (XRD) technique was used to access the crystalline nature of the coatings. This analysis was performed on a XPERT-PRO diffractometer in blazng angle mode with 2θ between 20° and 80°. Topographic analysis was done using a 3D optical profilometer (Sensofar S-neox) to assess the surface roughness of the plasma-treated coated materials. Data were obtained with a 10 × interferometric objective (acquisition area of 1.75 mm × 1.35 mm) using the vertical shift interferometry technique (VSI). The visualization of the surface texture was also done using a higher magnification (100 × objective – acquisition area of 350 μm × 270 μm) under confocal mode. Finally, Raman spectra were obtained for these CrN coatings on a confocal Raman-AFM-SNOM WITec alpha300 RAS+ microscope. The excitation source was the 532 nm line of a Nd:YAG laser with 5 mW incident power on the samples. The spectra were obtained in the Stokes shifts interval between 80 and 2000 cm^{−1}.

Open circuit potential (OCP) measurements were performed in a 0.9% NaCl solution for 3 h to mimic the performance of the more promising coatings deposited in glass slides and PET in high humidity and saline environments, using a saturated calomel electrode (SCE) in a Gamry Reference 600 potentiostat (Gamry Instruments Inc., PA, USA). The color coordinates of the films were measured in the silicon < 100 > substrates, using a Minolta CM-2600d portable spectrophotometer equipped with a 52 mm diameter integrating sphere and 3 pulsed xenon lamps and a wavelength range of 400–700 nm. The color coordinates were measured in ABS pieces provided by the end-user and were represented in the CIELab-1976 color space at a viewing angle of 10° and using the primary illuminant D65 (specular component included – SCI). Flat PET substrates were used for the cross-cut tape test on the film that best complied with the end-user specifications, based on the ASTM D3359-B standard.

3. Results and discussion

3.1. Morphological, microstructural and chemical characterization

The morphological features of the sputtered CrN samples from series #1 and #2 are present in Figs. 1 and 2, respectively. For the pure Cr reference sample it is possible to observe the occurrence of a typical elongated granular morphology, Fig. 1a [28]. The resulting morphology is quite rough ($S_a = 42$ nm, Fig. 3a) and consists of a highly oriented and crystalline Cr (210) growth (card #65-3316), Fig. 4a.

By introducing small amounts of nitrogen (2 and 3 sccm) in the system, round granular morphologies are obtained [28–30], Fig. 1b–c. Since the obtained surfaces are dense and very smooth [30] ($S_a \approx 21$ nm for both samples, Fig. 3a) the magnification of Fig. 1c is higher in order to observe the round granules. Due to the low nitrogen amount (nitrogen composition ≈ 17 at.%), a low-crystallinity microstructure – slight nitrogen incorporation in the chromium matrix (the broad peak at $\approx 42^\circ$ corresponds to the Cr₂N (002) phase, card #35-803) – is obtained for the 2 sccm N₂ sample, while an almost amorphous growth is visible for the 3 sccm N₂ film, Fig. 4a. With further nitrogen increase (4 sccm), the surface morphology of the samples starts to change, and the smooth, granular features become increasingly sharp and angular, Fig. 1d. As a result, the roughness slightly increases ($S_a \approx 26$ nm, Fig. 3) due to an increasingly N-rich crystalline Cr₂N (002) preferential growth, Fig. 4a.

For high nitrogen flow rates, higher nitrogen incorporation occurs (≈ 29 and 25 at.% for 6 and 8 sccm, respectively – Table 1). Consequently, evidence of pyramid-like column tops (typical for high N₂ contents [31]) starts to appear in the sample sputtered with 6 sccm and

Download English Version:

<https://daneshyari.com/en/article/8023339>

Download Persian Version:

<https://daneshyari.com/article/8023339>

[Daneshyari.com](https://daneshyari.com)