Applied Surface Science 271 (2013) 113–117

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Critical tuning of magnetron sputtering process parameters for optimized solar selective absorption of $NiCrO_x$ cermet coatings on aluminium substrate

Lucie Gaouyat[a,*], Frédéric Mirabella[b], Olivier Deparis[a]

[a] Solid State Physics Laboratory, Research Center in Physics of Matter and Radiation (PMR), Facultés Universitaires Notre-Dame de la Paix (FUNDP), 61 rue de Bruxelles, B-5000 Namur, Belgium
[b] CRM Group – AC&CS, 57b boulevard de Colonster, B-4000 Liège, Belgium

ARTICLE INFO

Article history:
Received 19 July 2012
Received in revised form 11 October 2012
Accepted 21 January 2013
Available online 8 February 2013

Keywords:
Magnetron sputtering deposition
Cermet material
Reflectivity modelling
UV–vis–NIR reflectivity
Composition analysis
Surface morphology

ABSTRACT

$NiCrO_x$ ceramic–metal composites (i.e. cermets) exhibit not only oxidation and moisture resistances, which are very important for industrial applications, but also remarkable solar selective absorption properties. In order to reach the best optical performances with only one coating layer, tuning of the magnetron sputtering process parameters (O_2 flow rate, pressure and deposition time) was performed systematically. The process window turned out to be very narrow implying a critical tuning of the parameters. The optimal operating point was determined for a single layer coating of $NiCrO_x$ on an aluminium substrate, leading to a spectrally integrated solar absorption as high as 78%. Among various material properties, the focus was put on the optical reflectance of the coating/substrate system, which was measured by UV–vis–NIR spectrophotometry. Using complex refractive index data from the literature, the theoretical reflectance spectra were calculated and found to be in good agreement with the measurements. Chemical analysis combined with scanning electronic and atomic force microscopies suggested a cermet structure consisting of metallic Ni particles and a compound matrix made of a mixture of chromium oxide, nickel oxide and nickel hydroxide.

1. Introduction

The $NiCrO_x$ ceramic–metal composite (i.e. cermet) has specific characteristics in terms of magnetic [1] and electrical [2] properties. However, its optical properties are by far the most attractive ones because of absorption/emission spectral selectivity [3]. Therefore, in order to reach a high selective absorption of the solar spectrum with a cermet coating on a metal substrate, one must simultaneously minimize the reflectance in the UV–vis–NIR range and keep the reflectance high (i.e. emissivity low) in the (thermal) infrared range where the coating is assumed not to modify the reflectance of the metallic substrate. This article focuses on the optical properties of the coating/substrate system in the UV–vis–NIR range. The selectivity in this wavelength range can be described by a quantity called the solar absorption α [4], which represents the fraction of the solar spectrum that is effectively absorbed by the system. It is calculated by: $\alpha = \int [1 - R(\lambda)]B_{sun}(\lambda)d\lambda / \int B_{sun}(\lambda)d\lambda$, where $R(\lambda)$ is the reflectance and $B_{sun}(\lambda)$ is the normalized Air Mass 1.5 (AM 1.5) solar irradiance spectrum, which corresponds to the irradiance of the sun (blackbody at 5000 K) taking atmosphere absorption bands into account. Note that the absorption spectrum $A(\lambda)$ is equal to $1 - R(\lambda)$ because the transmittance spectrum $T(\lambda)$ of the coated metallic substrate is equal to zero in the wavelength range of interest (i.e. $A = 1 - R - T$ with $T = 0$). Understanding the physical origin of the solar selective absorption/emission is a challenging task involving multiscale characterization, from macroscopic optical reflectance measurements to micro/nanostructure observations. In this article, the influence of reactive magnetron sputtering deposition parameters (deposition time, O_2 flow rate and pressure) on the material elementary composition and its optical reflectance was systematically studied, respectively using Rutherford backscattering spectroscopy (RBS) and UV–vis–NIR spectrophotometry. The optical properties are known to be strongly dependent on the deposition parameters. A slight change in the reactive atmosphere e.g. O_2 flow rate) can lead to very different optical constants of the material (complex refractive index), see for example [5]. Consequently a process window has to be found in order to synthesize samples with desired performances. This is the strategy we adopted in our study, as it will be described hereafter. Further chemical analysis by X–ray photoelectron spectroscopy (XPS) was performed in order to determine the oxidation state of each element composing the coating material. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) micrographs of typical samples were analysed, revealing the existence of a granular

* Corresponding author. Tel.: +32 81724710.
E-mail address: lucie.gaouyat@fundp.ac.be (L. Gaouyat).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.01.136

Table 1
Oxygen flow used to prepare the samples.

O_2 flow (in sccm)	0.7	1.5	1.8	2.0	2.2
Low pressure (6.9×10^{-3} mbar)		X	X	X	X
High pressure (1.4×10^{-2} mbar)	X			X	

nanostructure. The optimization of the sputtering parameters enabled the deposition of a segregated material, which exhibited the desired absorption selectivity in the UV–vis–NIR range.

2. Experimental and modelling methods

The $NiCrO_x$ coatings were deposited from a NiCr target (76 mm diameter, 5 mm thickness, 80% Ni +20% Cr 99.9% purity from Neyco) on 0.3-mm thick laminated aluminium (Al) substrates (from Alcan) by DC reactive magnetron sputtering in a Kurt J. Lesker CMS 18 chamber at room temperature with a base vacuum between 1.3×10^{-7} mbar and 1.3×10^{-8} mbar. Due to lamination, the substrates exhibited sub-micron size roughness. This feature provided our samples with quite different characteristics in comparison with previously reported coatings on flat substrates. The deposition chamber was coupled with a glove box, linked by a commercial mechanical arm so as to ensure a permanent high vacuum and avoid impurities inside the chamber. Layer thicknesses were measured by separate calibration tests on flat silicon (Si) substrates using a Veeco Dektak 6 M Stylus profilemeter with a diamond tip (12.5 μm radius of curvature). The deposition was performed at a constant electrical power (200 W) and the influence of two deposition parameters (pressure and O_2 flow rate) was systematically investigated as shown in Table 1.

The duration of the deposition was calibrated in order to reach a coating thickness of 70 nm ± 5 nm for all samples (samples of 90 nm ± 5 nm thickness were however fabricated for specific purposes, see next section). RBS measurements were performed at 165° and 170° angles using a 2.9 MeV He^+ beam produced by a 2 MV Tandetron (*R*) particle accelerator. Depth profiles were extracted thanks to the SIMTarget 1.0 code [6]. The optical reflectance measurements were performed using a UV–vis–NIR Perkin Elmer lambda 950 spectrophotometer equipped with a 150-mm integrating sphere. The SEM micrographs were obtained using a Jeol 7500 F SEM. AFM observations were performed in ambient air using a commercial AFM instrument (Dimension 3100, Digital Instruments). The tapping-mode was used with standard unmodified silicon cantilevers of 7-nm curvature radius and 42 N m^{-1} spring constant (nominal values). Topographic AFM images were recorded at a scanning rate of 1–2 Hz and a resonance frequency of about 300 kHz (nominal value). The background slope was resolved using first-order polynomial function. No further filtering was performed. The XPS spectra were recorded using a PHI-Quantum 2000 XPS instrument. The XPS data were collected with a hemispherical electron energy analyzer. XPS spectra were obtained using monochromatic Al Kα X-rays (1486.69 eV) with the X-ray source operating at 20 W after a 120-s sputtering under Ar^+. Data analysis was performed using WinSpec software developed in Namur University. Shirley backgrounds were used in the peak fitting. Quantification of XPS spectra used relative sensitivity factors supplied with the instrument. The modelling of the spectral reflectance of the coated substrates was achieved thanks to a standard electromagnetic code, which solved Maxwell's equations in arbitrarily stratified isotropic optical media [7]. Determining the complex refractive indexes of such heterogeneous material by spectral ellipsometry is challenging, especially for $NiCrO_x$ material for which reported index data are very scarce. Therefore, in our reflectance modelling, we used $NiCrO_x$ refractive indexes from the literature [5]. For the Al substrate, we used standard refractive index from the literature [8].

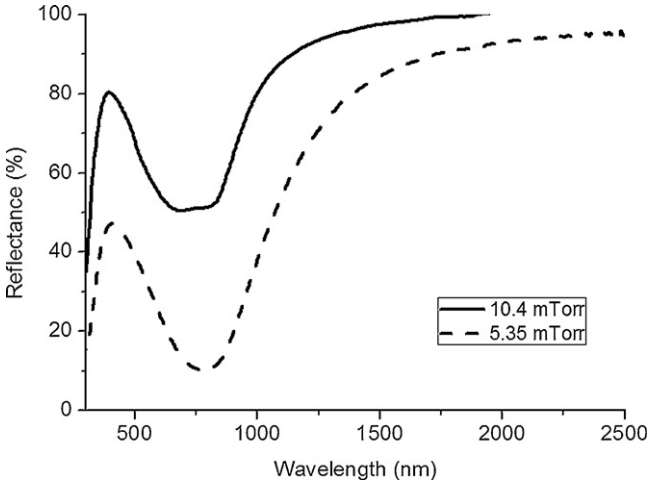

Fig. 1. Experimental reflectance spectra of samples deposited at different pressures: 1.4×10^{-2} mbar (solid line), 6.9×10^{-3} mbar (dashed line). O_2 flow rate was equal to 1.8 sccm in both cases.

Our calculations took into account both polarisation components of the incident light in equal proportions. Normal incidence of the light was assumed.

3. Results and discussion

The deposition parameters had a huge influence on the optical properties of the $NiCrO_x$ coatings. A slight change in the atmosphere composition led to completely different reflectance spectra. Therefore, measurements of reflectance spectra were useful for investigating the effects of deposition parameters, such as O_2 flow rate. The influence of the pressure on the reflectance was also investigated. Two working pressures were used (6.9×10^{-3} mbar, 1.4×10^{-2} mbar), all other parameters being kept constant. Again, dramatic changes in the reflectance spectra were observed (Fig. 1). Such a behaviour was expected since a higher pressure implied more oxygen into the chamber during deposition and, as a result, the reflectance spectrum of the coating deposited at a higher pressure had the typical features of a more oxidized sample, according to simulations with the refractive indexes from Zhao et al. [5]. Still the difference in reflectance spectra between the two samples was huge for such a slight change in the deposition atmosphere (pressure).

Nevertheless, the most influent parameter turned out to be the O_2 flow rate, which was varied within a narrow range, from 1.5 sccm to 2.2 sccm (Fig. 2). The shape of the reflectance spectrum was radically modified according to the O_2 flow rate used during deposition. Within a very narrow O_2 flow rate range, a tuneable wavelength-selective reflectance was achieved. By depositing a layer of $NiCrO_x$ while tuning the O_2 flow rate, the reflectance of the metallic (Al) substrate was turned into the reflectance of a low-reflection coating in the UV–vis–NIR region. In this $NiCrO_x$/Al system, a wavelength-selective absorption could therefore be obtained.

Moreover, the deposition time (coating thickness) had an influence on the reflectance spectrum (Fig. 3a). The thicker the coating, the higher the displacement of the reflectance minimum towards longer wavelengths (red shift). A difference in thickness as small as 20 nm led to a wavelength shift as large as 300 nm. This means that the optical properties were very sensitive to tiny changes in deposition time (255 s and 328 s for the 70-nm and 90-nm thick samples, respectively). The shift of the reflectance spectrum according to the coating thickness is well known from wave optics theory applied