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Characterization of perovskite film prepared by pulsed laser deposition on ferritic stainless steel using microscopic and optical methods

E. Durda [a,*], J. Jaglarz [b], S. Kąc [c], K. Przybylski [a], Y. El Kouari [d]

[a] Faculty of Materials Science and Ceramics, AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Krakow, Poland
[b] Faculty of Mechanics M2, Cracow University of Technology, Al. Jana Pawła I37, 31-864 Krakow, Poland
[c] Faculty of Metals Engineering and Industrial Computer Science, AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Krakow, Poland
[d] Electrical Engineering Department, Faculty of Science and Technology Mohammedia, University Hassan II of Casablanca, Morocco

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ABSTRACT

The perovskite $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF48) film was deposited on Crofer 22 APU ferritic stainless steel by pulsed laser deposition (PLD). Morphological studies of the sample were performed using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Information about film thickness and surface topography of the film and the steel substrate were obtained using following optical methods: spectroscopic ellipsometry (SE), bidirectional reflection distribution function (BRDF) and total integrated reflectometry (TIS). In particular, the BRDF study, being complementary to atomic force microscopy, yielded information about surface topography. Using the previously mentioned methods, the following statistic surface parameters were determined: root-mean square (rms) roughness and autocorrelation length by determining the power spectral density (PSD) function of surface irregularities.

1. Introduction

Ferritic stainless steels (FSS) are widely used in various industries due their excellent properties, such as: high resistance to thermal fatigue and stress corrosion cracking, high toughness, ductility and weldability, especially in comparison with conventional austenitic stainless steels [1–3]. An important advantage of FSS is high oxidation resistance. FSS with high Cr content (>13 wt.%) at elevated temperatures form a protective oxide scale consisting of inner layers built of chromia and a thinner outer layer consisting of the $MnCr_2O_4$ spinel [4].

However, long-term oxidation of this type of steel leads to some undesirable phenomena, such as deterioration of its electrical properties caused by gradual increase in area specific resistance (ASR) due to the growth of a Cr_2O_3 scale, as well as evaporation of volatile chromium compounds [4–7]. These are important aspects in terms of potential applications of these steels. Ferritic stainless steels are intensively studied as potential interconnect materials for solid oxide fuel cells (SOFC) that operate in the intermediate temperature range (600–800 °C) [4,5,8,9]. In order to limit the above-mentioned negative effect, protective-conducting coatings are applied on the surface of the steel [10].

Among the wide group of materials used as protective coatings, one of the most promising are perovskites, which are described by the general formula of ABO_3, where A is a large trivalent rare earth cation (e.g., La or Y) and B is usually a trivalent transition metal cation (e.g., Cr, Ni, Fe, Co, Cu or Mn) [10]. Partial substitution of the A-site cations by large earth alkali cations (e.g., Sr and Ca) and, in addition, of the B-side by electron acceptors (e.g., Ni or Fe) leads to an increase in conductivity by up to two orders of magnitude [11].

The most common methods of applying coatings on steel include e.g. screen printing, sol–gel techniques, plasma spraying, radio frequency magnetron sputtering and electrodeposition [10]. However, a fully dense, uniform coating with a good adhesion to the metallic substrate is not obtained from most of these methods. From this point of view, pulsed laser deposition (PLD) seems to be promising technique for preparation of protective coatings on interconnectors. The advantage of PLD is that the stoichiometry of the target can be transferred directly to a film, even in the case of targets with complicated chemical compositions [12]. Due to the inherent advantages of PLD, the method is suitable for production of thin films of semiconductors, diamond-like structures and films for photonic applications [13–15].

There are only a few reports concerning the use of the PLD technique for deposition of protective coatings on metallic interconnects [16–18]. In those works, only results of oxidation resistance and ASR measurements were presented, however no data was

* Corresponding author.
E-mail address: edurda@agh.edu.pl (E. Durda).

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given concerning the characteristic of the films after deposition. The evaluation of quality and physical parameters of the film is an important aspect in term of steel/film composite properties, e.g. high temperature corrosion or electrical properties.

In this study, the $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF48) perovskite was used as a protective coating material. The LSCF48 film was deposited on the ferritic stainless steel with the trade name 'Crofer 22 APU' by the pulsed laser deposition technique.

The goal of this work was to determine the topography of the LSCF48 film and the correlation between surface parameters of the substrate and the film. In these studies, next to conventional microscopic techniques (AFM, SEM), optical methods, such as spectroscopic ellipsometry, bidirectional reflection distribution function and total integrated reflectometry, were used. Optical techniques allowed for the extension of the wavelength range to longer space wavelengths and for obtaining a description of the film topography over a wider area than microscopic method (e.g. AFM).

2. Surface roughness description

Fora quantitative depiction of the surface topography, the roughness power spectral density (PSD) function is used, which describes most real surfaces as a function of statistical parameters. PSD expresses roughness power per unit roughness frequency over the sampling length [19]. From a mathematical point of view, PSD is a Fourier transform (FT) of the surface profile $h(r)$ and is expressed in the spatial frequency domain f, which is defined as inverse spatial wavelength.

The PSD function is commonly evaluated by processing data obtained by a mechanical profilometer and/or AFM images [20]. If the values of PSD are known, one can determine the statistical parameters, such as the root-mean square (rms) roughness σ, slopes and the autocorrelation length by using the so-called *ABC* model which describes PSD of a random surface in a simple analytical equation [19]:

$$PSD(f) = A\left[1 + (Bf)^2\right]^{-C/2} \tag{1}$$

where *A*, *B* and *C* are model parameters related to basic quantities characterizing a surface, i.e. *A* is a PSD value for low frequency, $B/2\pi$ is the correlation length and *C* determines the type of power law in high spatial frequency and qualifies the type of random distribution of irregularities.

Formula (1) was used to determine statistical surface parameters as root mean square (rms) roughness σ and correlation length *L*.

3. Experimental procedure

3.1. Sample preparation

The $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF48) powder was prepared by the auto-ignition technique. Combustion synthesis is a processing technique that can produce oxide materials via an exothermic reaction between dissolved metal nitrates (oxidizing agent) and an organic fuel (reducing agent; urea in the present case). LSCF48 precursor materials were then calcined at 1100 °C for 3 h. The powder was supplied by Marion Technologies S.A., Toulouse, France [21].

Crofer 22 APU ferritic stainless steel (ThyssenKrupp VDM GmbH, Germany) was used as a substrate material. The chemical composition of this steel is presented in Table 1. Samples with dimensions of about $10 \times 10 \times 0.5$ mm were ground with 100–1200-grid SiC papers, then polished with an alumina slurry and finally ultrasonically cleaned in acetone.

LSCF48 film was obtained using pulsed laser deposition (PLD). The target for PLD was prepared by compacting the LSCF48 powder under 300 MPa. The pellet was then sintered in air at 1200 °C for 2 h. The final diameter and thickness of target were: 30 mm and 5 mm, respectively.

The film was deposited using a Nd:YAG laser (Coninuum, Powerlite Precision II 9010 DLS) of 266 nm wavelength, 100 mJ laser pulse energy, 9.7 J/cm^2 energy density and 10 Hz frequency. The deposition was performed at a substrate temperature of 300 °C, an oxygen partial pressure of 5 mTorr and target-substrate distance of 70 mm. The film was deposited by 180,000 laser ablation pulses.

3.2. Measurement techniques

Morphological observations of the sample were carried out via scanning electron microscopy (SEM) using a FEI Nova NanoSEM 200. AFM experiments were carried out using a NTEGRA Aura (NT-MDT) atomic force microscope. Images were acquired at a resolution of 256×256 points.

The total reflectance spectrum was measured using a Perkin–Elmer Lambda 900 spectrophotometer equipped with an integrating double-beam sphere of 120 mm diameter [22]. The reflectance measurements were performed in a wavelength range of 250–2500 nm with a mean step of 2 nm.

For determination of samples roughness the total integrated scatter method (TIS) was used. In this technique the intensities of the diffusively scattered light I_{diff} and light totally reflected from the samples I_0 are determined. For relatively flat surfaces the following formula is fulfilled [23]:

$$I_{diff} = I_0\left(\frac{4\pi\sigma}{\lambda}\right)^2 \tag{2}$$

where λ is light wavelength.

For TIS measurements the ISP-REF-7 (Avantes Co.) integrating sphere was used. The laser diode with wavelength $\lambda = 635$ nm was applied as a light source.

In order to determine the thickness of the LSCF48 film and also refractive (n) and extinction (k) indices, the spectroscopic ellipsometer M-2000 (J.A. Woollam Co., Inc., USA) [24], operating in the spectral range of 190–1700 nm, was used. The sample was measured for three angles of incidence (65°, 70°, 75°). Additionally, in one experiment, the intensity of reflected light and the depolarization coefficient were measured simultaneously. In this study, the incident beam was linearly polarized with electric vector $\boldsymbol{E}$ inclined at 45° to the plane of incidence. One polarization component, the electric vector, $\boldsymbol{p}$, was lying in the incidence plane and the other, $\boldsymbol{s}$, was perpendicular to the plane. After reflection from the sample, the polarization changes to elliptical. The polarization ellipse can be described by two angles: Ψ representing the angle determined from the amplitude ratio between *p*- and *s*-polarizations and Δ is the phase shift between the polarized waves. The expressions Ψ and Δ are used in the following fundamental ellipsometric equation [25]:

$$r_p/r_s = \exp(i\Delta) \cdot \tan\Psi \tag{3}$$

where r_p and r_s are complex Fresnel reflection coefficients for '*p*' and '*s*' polarizations, respectively. By fitting the optical model of film to Eq. (3), film thickness (d), as well as the dispersive relations for $n(\lambda)$ and $k(\lambda)$ in a selected spectral range, can be determined. The data was analyzed using Complete EASE 5.0 software. In order to analyze ellipsometric data, Ψ and Δ angles, spectra were fitted for three angles of incidence (65°, 70°, 75°), simultaneously. Furthermore, interface roughness was measured using spectroscopic ellipsometry.