Applied Surface Science 321 (2014) 560–565

Contents lists available at ScienceDirect

Applied Surface Science

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

Femtosecond laser surface structuring and oxidation of chromium thin coatings: Black chromium

L. Kotsedi[a,b,*], Z.Y. Nuru[a,b], P. Mthunzi[c], T.F.G. Muller[d], S.M. Eaton[e], B. Julies[d], E. Manikandan[a,b], R. Ramponi[e], M. Maaza[a,b]

[a] UNESCO-UNISA Africa Chair in Nanosciences-Nanotechnology, College of Graduate Studies, University of South Africa, Muckleneuk Ridge, P.O. Box 392, Pretoria, South Africa
[b] Nanosciences African Network (NANOAFNET), iThemba LABS-National Research Foundation, 1 Old Faure Road, Somerset West 7129, P.O. Box 722, Somerset West, Western Cape, South Africa
[c] National Laser Centre, Council for Scientific and Industrial Research, 0001 Pretoria, South Africa
[d] University of the Western Cape, Physics Department, Bellville, 7535 Cape Town, South Africa
[e] Physics Department, Politecnico di Milano, Piazza Leonardo Da Vinci, 32, 20133 Milano, Italy

ARTICLE INFO

Article history:
Received 12 May 2014
Received in revised form 28 August 2014
Accepted 26 September 2014
Available online 5 October 2014

Keywords:
Chromium oxide
Laser irradiation
Laser surface structuring
Femtosecond regime
Solar absorbers

ABSTRACT

In view of their potential applications as selective solar absorbers, chromium coatings on float glass substrates were nano/micro structured by femtosecond laser in air. Raman and X-rays diffraction investigations confirmed the formation of an ultra-porous α-Cr_2O_3 layer at the surface; higher is the input laser power, enhanced is the crystallinity of the α-Cr_2O_3 layer. The α-Cr_2O_3 layer with the Cr underneath it in addition to the photo-induced porosity acted as a classical ceramic–metal nano-composite making the reflectance to decrease significantly within the spectral range of 190–1100 nm. The average reflectance decreased from 70 to 2%.

1. Introduction

Recently, ultrafast laser surface structuring in the sub-picosecond regime is gaining an important momentum within the solar energy field specifically for its capabilities in engineering large and effective selective solar absorbers [1]. In addition, these controlled nano-structured surfaces of metallic materials are adequately ultimate for additional applications such as thermophotovoltaics, thermal radiation sources, and radiative heat transfer devices among others [1–20]. In this regard, the comprehensive work of Vorobyev and Gao who have developed a cost effective femtosecond laser surface structuring technique, has allowed to transform highly reflective metals to either totally absorptive or reflecting surfaces [21,1,22–24]. Among this family, one should mention the case of aluminum (Al), titanium (Ti), tungsten (W), copper (Cu), and Ti alloy ($Ti_{90}/Al_6/V_4$)) as well as stainless steel (SS) which are materials widely used in many applications in the fields of renewable energy and solar energy efficiency. In the entire UV–vis–NIR wavelength range, the absorptance of the blackened metals was demonstrated to reach significant values about ~85–95% in a large solar spectrum range. The laser surface approach allows to produce a blackened area as small as a tightly focused laser spot, i.e. down to the laser beam waist of 10 μm, or as large as needed with a scanning laser beam configuration. An additional green advantage of this technique is its environmental benefit as it does not use any direct chemical regent. Moreover, such a surface nano-structuring can be achieved at standard conditions (no vacuum, at room temperature and atmospheric pressure conditions) as well as under various gas atmospheres. For the selective solar absorbing surfaces specifically, the previous studies concluded that the enhanced absorption of the dark metallic surfaces is caused by a rich variety of nano/microscale surface morphology coupled to the photo-assisted surface oxidation [1].

As it is established, black chromium which is in fact a chromium–chromium oxide nano-composite (Cr–Cr_2O_3) is one of the most commercially available medium temperature selective solar absorbers. For such a purpose, thin films of chromium metal deposited on various type of substrates of choice have been

* Corresponding author at: UNESCO-UNISA Africa Chair in Nanosciences-Nanotechnology, College of Graduate Studies, University of South Africa, Muckleneuk Ridge, P.O. Box 392, Pretoria, South Africa. Tel.: +27 8431145.
E-mail addresses: Kotsedi@tlabs.ac.za, lkotsedi@gmail.com (L. Kotsedi).

http://dx.doi.org/10.1016/j.apsusc.2014.09.168
0169-4332/

oxidized using laser sources in addition to a large variety of physical and/or chemical methodologies. In the case of laser assisted processes, the surface oxidation have been carried out using CO_2 continuous laser (cw) [25,26] whereby pure amorphous chromium thin films were deposited on KCl crystal, then irradiated with the cw CO_2 laser source in an open atmosphere, resulting in a Cr_2O_3 films. Likewise, Lain et al. [28,29] used Nd-YAG (1064 nm wavelength) source to irradiate Cr thin films on passivated Si substrates in an ambient environment with fluencies ranging from 15 to 100 mJ/cm^2. The resulting Cr_2O_3 had an (1 1 6) predominant planes orientation which is different from the standard texture observed when chromium is oxidized using non-laser surface structuring based approach. In this study, and comparatively to previous studies within the literature, an ultrafast laser source in the sub-picosecond regime has been used. More precisely, a femtosecond fiber laser was used to irradiate Cr thin films deposited on glass substrates with the aim of oxidizing their surface and study their surface morphology, microstructure as well as their optical properties in view of their usage as large selective solar absorbers in the CSP field.

Femtosecond laser microstructuring has been recently used to turn shinny, highly reflective metals like gold, silver, copper and others into either a black non-reflecting material or selectively reflecting materials. These selective reflection materials can be tailored such that they can absorb at specific wavelengths depending on the experimental parameters used during the microstructuring process [1]. This comes about when an ultrafast laser is used to ablate parallel grooves on the surface of a highly reflecting material and forming a reflective grating like phenomena. When the electromagnetic radiation strikes the now micromachined surface, the grooves on the surface reduces the reflectivity by trapping the incident light in their grooves [1,21]. This process of fabricating selective and totally absorbing material is a combination of processes, whereby the incident light is being trapped by the resultant material due to plasmonic effects, grating phenomena and the type of a metal oxide formed during laser interaction with the metal.

2. Experimental details

The Cr thin film coatings on standard cleaned float glass substrates were produced using the e-beam evaporation process. Prior deposition, the e-beam chamber was evacuated to reach an initial vacuum of 10^{-7} mbar as a base pressure before depositing the thin films of Cr at room temperature. The deposition deposition rate and total thickness of the Cr layers were ~1 nm/s and ~1 mm respectively. A femtosecond fiber laser pulsing at the fundamental wavelength of 1064 nm, repetition rate of 78.5 MHz and pulse duration of 290 fs was used to surface structure the thin films of chromium deposited on float glass substrates using the electron beam evaporation process. The samples were then mounted on an *X*–*Y* motorized stage programmed to execute an *X*–*Y* translations in a form of parallel lines while the laser was irradiating perpendicularly the sample with a waist of about ~100 μm above the sample in order to avoid excessive ablation of the chromium thin film coatings but only sufficient to apply enough energy to surface structure and oxidize the thin film coatings in air and transform them in oxide based materials. Follwing a surface morphological investigation using high resolution scanning electron microscopy, the crystalline structure of the laser surface structured Cr films were investigated using a X-ray diffractometer (XRD, model Bruker AXS D8 Advance, $K\alpha_1$ line of copper $\lambda = 1.5406$ Å) in view of confirming the existence of chromium oxide if any. Likewise, Raman spectroscopy investigations were conducted to identify the nature of oxide Cr_xO_y. This was conducted using a Horiba Jobin Yvon Raman unit (LabRAM HR UV/vis/NIR). Their surface morphology was investigated using a Leo-StereoScan 440 scanning electron microscope (HRSEM).

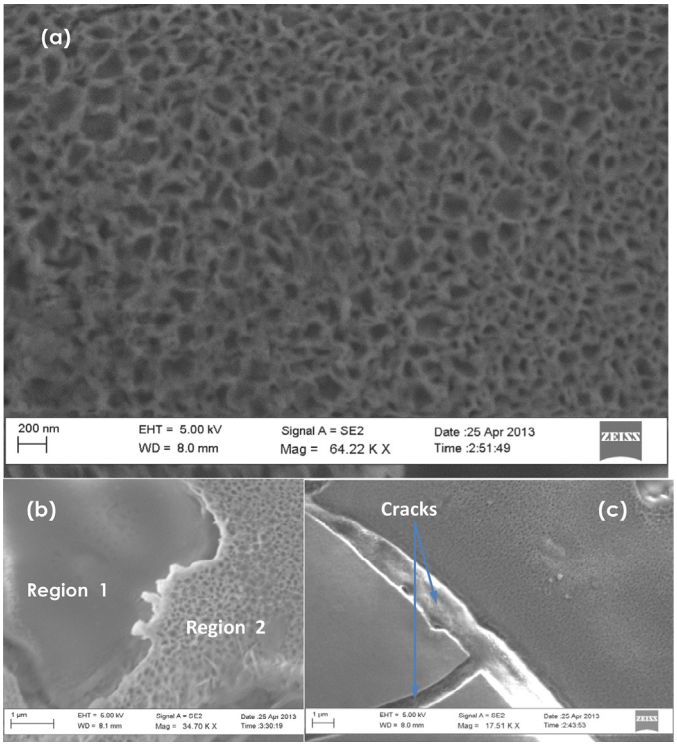

Fig. 1. Typical high resolution scanning electron microscopy of the femtosecond laser structured Cr coatings onto float glass substrate: (a) below the threshold input laser power, (b) above the threshold value inducing the ablation of the film as reported in region 1 and (c) stress induced cracks in the Cr coating.

3. Results and discussion

Fig. 1 reports a typical high resolution scanning electron microscopy (HRSEM) micrograph of the laser irradiated coatings. Relatively to the smooth as deposited Cr thin film, the irradiated ones exhibit a significant morphological change as a result of the laser interaction with the Cr film. As observed from the micrographs, Fig. 1a specifically, the irradiated samples exhibit a sponge type meso-porous network. The average porosity is within the range of ~27–200 nm while the wall average thickness in between the porous regions is ~47 nm. This surface morphology trend seems to move toward being more porous as the laser power increases to ~250 mW. There is also some ablation phenomenon starting to take place as shown in region 1 of Fig. 1b at such laser powers. The evolution of the films as the laser power increases is clearly shown in the scanning electron microscope of the samples in Fig. 2. Above such a threshold, the ablation phenomenon starts to take place as shown in region 1 of Fig. 1b. Likewise and as reported in Fig. 1c, the laser irradiated surface starts to crack. Similar cracks have been observed in the laser irradiated film in the case of chromium and have been attributed to the lattice shrinking of the chromium [1 1 0] *d*-spacing beneath the oxidized Cr layer due to the induced stress in the film chromium during the oxide formation/growth. It is worth to mention that in other studies using laser sources operating in the nanosecond regime, the irradiated Cr surface exhibited a dense structure of nano-crystalline clusters. This latter photo-induced configuration was attributed to a grain boundary controlled oxidation process. Hence, it might that the observed meso-porous structure in this case be caused by a similar phenomenon.

To shed light on the nature of the surface layer formed during the laser–Cr surface interaction in open atmosphere which