Morphological and Optical Characterization of e-beam deposited anatase films to be used in Solar Thermal Collectors

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1. Abstract

This paper presents results obtained from the characterization of anatase selective surfaces to applications in solar collectors as well as a comparison with commercial selective surfaces. With the goal to authenticate Brazilian technology and/or a material with a low cost, expensive metal such as titanium and their oxides with high purity degree were replaced by a natural mineral based on titanium dioxide: anatase. Selective surfaces made of anatase were produced through e-beam at a pressure of 10^{-3} bar for 5 minutes. Images obtained by atomic force microscopy (AFM) and scanning electron microscopy (SEM) show nanostructured grains homogeneously distributed throughout the surface with diameter and height approximately 60 nm and 6 nm, respectively, and fractal dimensional of 2.10. Chemical analysis by EDX evidences the presences of Fe, Al, Ti, Si and their oxides homogeneously distributed. Optical absorbance of 85% points out that anatase surfaces hold efficiency in comparison to commercial surfaces.

2. Introduction

Nowadays there are three types of renewable energies capable of generating heat, they are: biomass, geothermal and solar. The first one, according to studies from AEE of 2009 (*Institute for Sustainable Technologies*), will be used for transportation, generation of electric energy and applications that require high temperature. The second one has geographic limitations, leaving solar energy as a promising choice for studying heat generation at average temperatures (up to 150^{o}C).

Nevertheless, to achieve the heat generation demand, especially to what is related to the generation of average temperature heat, solar energy industry calls for progress in research and development on three main fields: (i) new technologies on heat storage; (ii) new materials in order to increase solar collector efficiency; (iii) development of better systems to refrigerate the current solar collectors. The main point of this paper is to contribute to item (ii).

Due to the great growth in Brazilian economy in the last decade, a higher energy demand becomes more and more required. In a way to overcome a possible energy crisis, it is important to try to enhance the use of natural resources, mainly the solar irradiation. Recent researches reveal that, in Brazil, the biggest villain concerning residential energy consumption is the electric shower bath, going through roughly 25% of the total domestic energy demand and reaching up to 12% of the national demand from 6 P.M. to 10 P.M. In this context, the use of renewable energies comes along as an alternative to diversify the country energetic matrix in a way to reduce the dependence of the rain schedule and assist areas where the energy generation is still made through diesel.

Currently there is a large concern from Brazilian politics to lower the consumption of electric energy. In the two biggest cities of the country specific laws were made to demand solar energy use. In São Paulo, law 14459 states that every new building inside the city must provide the installation of solar water heating system. Also, law number 326 from 2007, obliges the installation of heating water system on every new public building inside São Paulo. In Rio de Janeiro, law number 5184 from 2008, obliges the installation of heating water system on new public buildings.

Solar irradiation rate in Brazil is higher when compared to other countries due to its extension and location. The country's commercial production of solar collector panels is however quite low due to its lack of technology, reducing its applications to only houses and pools. High efficient panels reach higher temperatures by using selective surfaces, raising the range of applications and covering industry need for efficiency when it comes to water heating, production of electricity through thermal cycles and even to supply small apartment complexes. Today is also being considered the possibility to use selective surfaces in air conditioned systems through thermal inversion.

According to E. E. Chain [Chain] selective surfaces are normaly composed of copper oxide, black nickel and other metal oxide films. They can be produced by electrodeposition, chemical deposition through spray pyrolysis or plasma techniques, according to A. G. Munõz and J. B. Bessone [Munõz et al] . The main feature of these surfaces is to provide high absorbance in the visible and ultra violet (UV) region of the spectrum to solar radiation and very low emittance in the infra-red region of the electromagnetic spectrum. More recently, different material combinations have been tested as selective surfaces with special interests in the development of micro or nano structured materials having small metallic particles dispersed in an oxide matrix [Oelhafen et al].

Not only for economical reasons but also looking for efficiency, various types of absorber coatings and preparations can be used for solar collectors [Lampert]. Titanium oxide thin films have been widely studied in numerous applications as it posses thermal and chemical stability. TiO_2 can exhibit different crystal structures: rutile, brookite and anatese [Tang et al]. Anatase comes across as a convenient choice due to its low cost when compared to commercial titanium and, in the specific case of Brazil, as it is easily acquired as a residue of the extractive industry.

During the following part of this work, results of the morphological, chemical and optical characterization of anatase selective surface are presented as well as a comparison between our surfaces and other commercials selective surfaces.

3. Experimental

3.1. Materials and Methods

Commercial grade aluminum was used as a substrate for this investigation. Sample pretreatment included mechanical polishing up to 1 μm diamond paste, resulting in a mirrored surface after mechanical polishing. The anatase concentrate was powdered and pressed at 8T resulting in tablets of ½ inch. The deposition chamber was evacuated to pressure of 10^{-6} bar and working pressure of 10^{-3} bar. The substrate was set in the holder at a distance of 100 mm from the base of the e-beam source. The film was deposited for 5 minutes.. The film was then coated with a thin layer of SiO_2. Analysis of the film thickness made by profilometry showed that the surfaces had a thickness of about 2.8 μm.

Surface morphology, roughness as well as the nonstructuration was analyzed by AFM (Microscopy Force Atomic) using JPK Microscope in intermittent mode and silicon tips from Micromash NCS16.

AFM images were analyzed by calculating roughness and fractal dimension by an algorithm developed by the Signal and Image Processing Laboratory of the Brazilian Center for Research in Physics (CBPF). This algorithm was divided into two parts: the first one computes the roughness based on the box-counting dimension technique [Lima et al]. Image was divided into a regular grid and the root-mean-square roughness calculated for each grid box. Then the size of the box was progressively reduced by a factor $s = 2^n/x$, where n={1,2,3,…} and x={1,2,3,…} and roughness, as a function of the box dimension, was computed. The roughness value was calculated by

$$R_m = \left(\frac{1}{n} \sum_{i=1}^{n} (x_i - \bar{x})^2 \right)^{\frac{1}{2}} \quad (1)$$

In the second part, a linear log-log fitting algorithm for evaluating roughness and box size was designed. The slope of the straight line fitted (angular coefficient) is the Hurst exponent [Lima et al]. Finally, the fractal dimension was computed using the following equation:

$$D_f = 3 - H \quad (2)$$

Elements presented on the surface were investigated by SEM (Scanning Electron Microscope) with EDX (Energy Dispersive X-Ray Analysis) in a FEI QUANTA 400. SEM Images were acquired with working distance of 10 mm, spot size 6,4 and high voltage of 25 kV.

Finally, optical characterization was accomplished by reflectance in the range of wavelengths of ultraviolet by UV-VIS (Ultraviolet and visible spectroscopy) and infrared by FTIR (Fourier transform infrared spectroscopy) in the range of 0.2 to 20 µm.

4. Experimental

The Figure 1 presents the topography and phase contrast images of anatase film deposited on aluminum as observed by AFM.

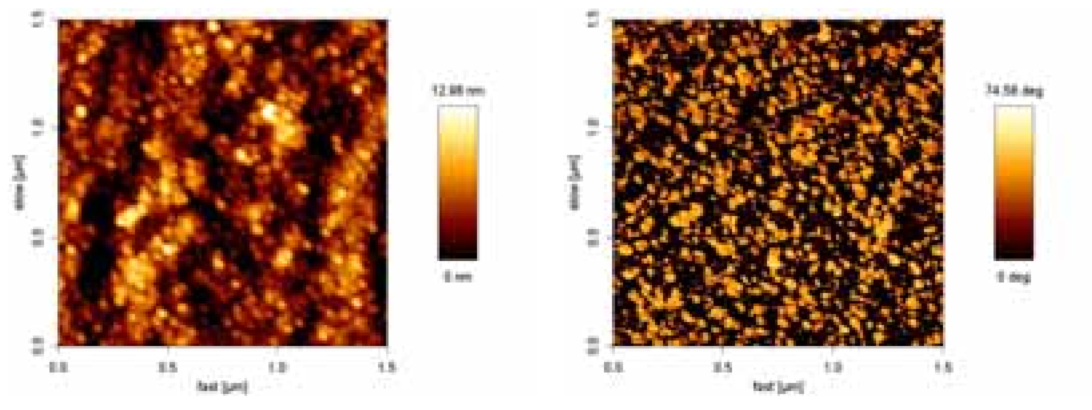


Figure 1. . Images of surface topography and phase contrast from selective surface of anatase deposited on polished aluminum and acquired by AFM.

It can be observed in the topographic image that grains are smoothly and homogeneously distributed on the surface. The grains have nanometric dimensions with circular geometry and a diameter of 60 nm and height of 6 nm.

Fig. 2 presents variation of the roughness with box size (log-log) for image of 10 µm and the Table 1 shows the results of morphological characterization of the selective surfaces from anatase films deposited on aluminum substrate.

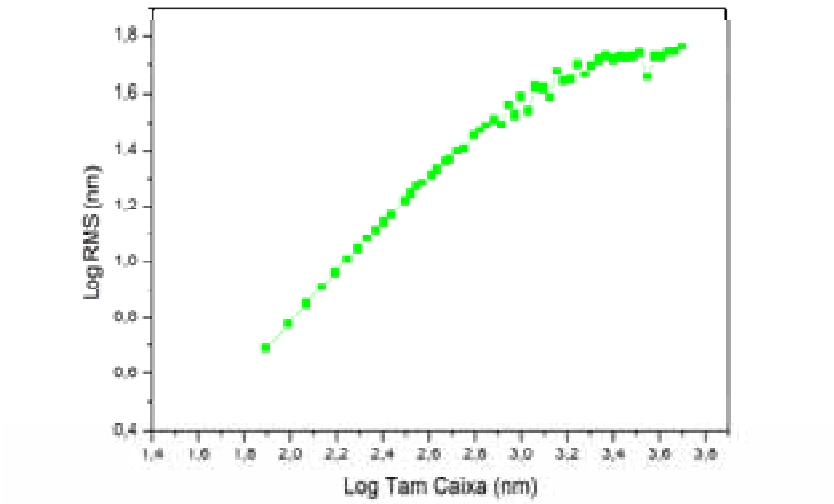


Figure 2. A log-log graph of box counting of the anatase film surface deposited on polished aluminum and acquired by AFM.

Table 1. Results of morphological analysis by AFM

Dimension (μm)	Roughness RMS (nm)	Maximum Height (nm)	Phase difference (deg)
10	18	63	40
2,5	3,5	15	68
1,5	3,0	13	75

It can be observed that roughness increases with the size of the image, however it is noted that in the image of 10 μm the roughness of surface reaches saturation, presenting a saturation roughness of 18 nm, at a box size of 3 nm, Fig.2.

Fractal dimensional was measured to be 2.10 and may be related with the formation of a bidimensional layer, with a few clusters that may be associated with the growth in preferential sites causing an increase in maximum height . It can also observed in the phase contrast image a variation of the stiffness of the sample related to the presence of the circular features. This variation may be caused due to the presence of several different materials with different atomic numbers and hardness organizing themselves in a nanostructed manner due to the lack of solubility, that does not allow the formation of a solid solution. This point deserves further study.

Scanning electron microscopy images acquired with higher magnification indicate that the film presents an homogeneous and faultless surface. The film is continuous with good adherence to the substrate in spite of its great thickness.

Figure 3 presents the typical results of the chemical analysis by energy dispersion spectroscopy (EDX) of the sample. There is an increasing aluminium presence as it is the substrate material. One also sees a strong presence of titanium homogeneously distributed on the film. It is also noted the presence of O, Mn, Mg, Fe, Zn, Zr, Si and Nb that are caused by the composition of anatase. This result is in agreement with the X-Ray diffraction (XRD) of the anatase original material. XRD of the film clearly indicates that the surface is mainly amorphous.

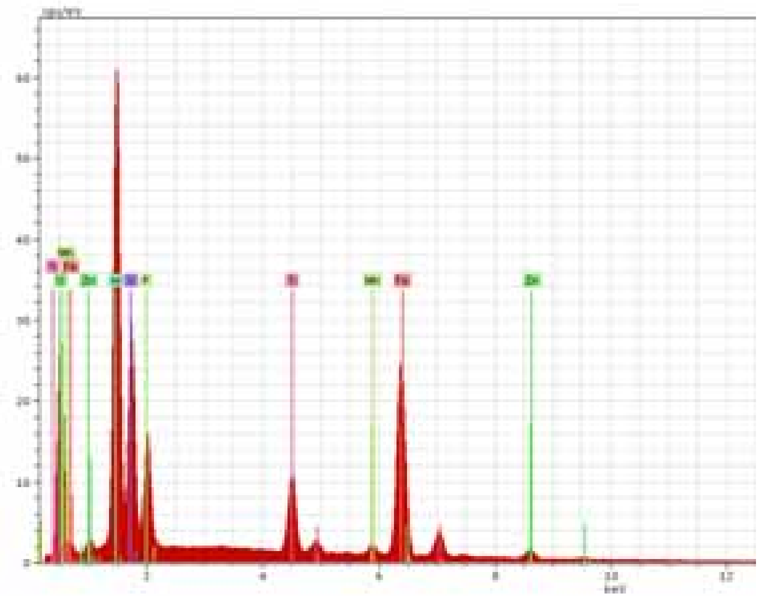


Figure 3. EDX analysis of selective surface of anatase.

Figure 4 shows the cross section of the selective surface as observed by SEM. It can be seen that, after the cutting and grinding of the sample, the film surface broke. Zooming in a intact part of the film, it can be observed that the surfaces produced have approximately 3 μm in thickness, value consistent with the thickness measured by perfilometry.

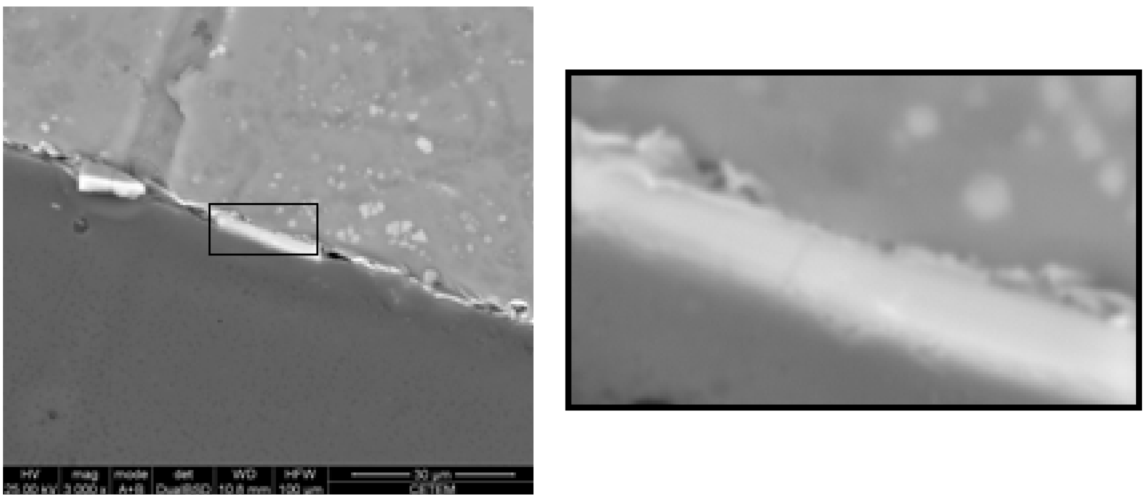
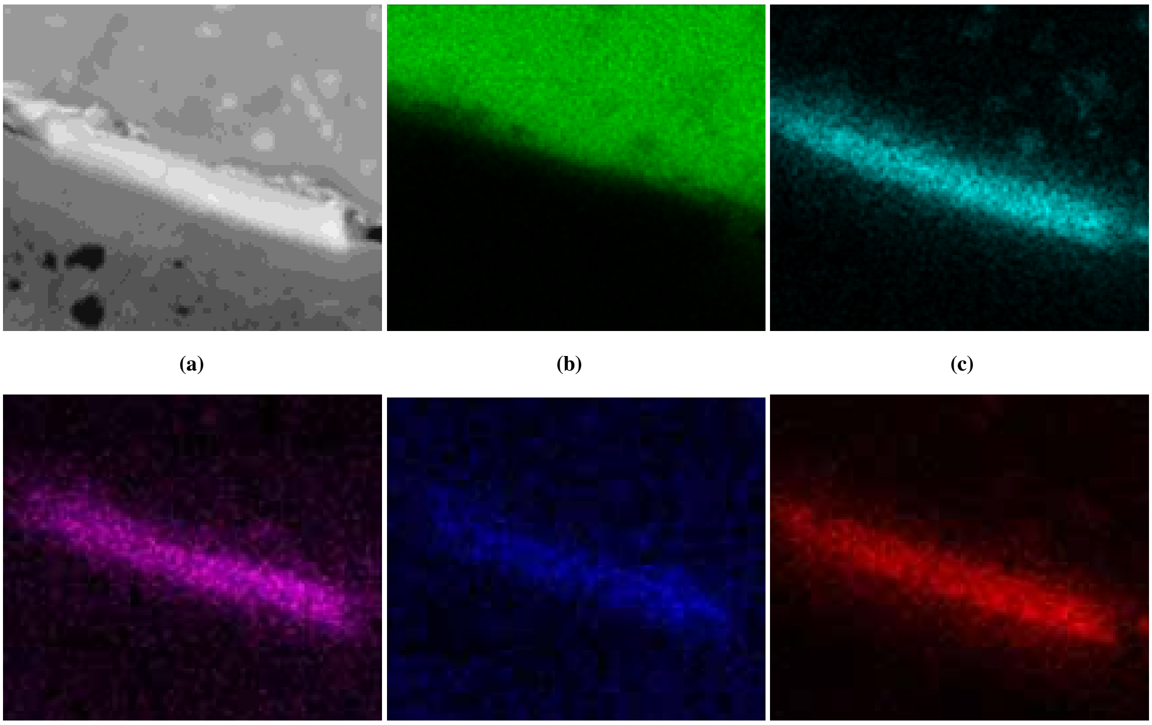


Figure 4. Images of the cross section of the selective surfaces of anatase by SEM.

In order to try to better understand the way the different phases were deposited, mapping images were acquired by EDX, and are presented in Figure 5. This technique allows the selection of some elements to map their distribution along the film. This acquisition was necessary because the deposition process can form irregular surfaces, making distinct layers as it deposits first the elements of lower boiling point.



(d) (e) (f)

Figure 5. Cross-sectional images of the surface of anatase by EDX selective. In (a) EDX image. Images of the mapping of aluminum (b) Iron (c) P in (d), silicon (e) and titanium (f).

By EDX mapping it can be seen that the anatase film was formed by metal and ceramic oxides distributed over the entire film thickness, most of the surface is composed by iron and titanium.

Figure 6 shows the optical characterization of the surfaces by UV-Vis and FTIR spectroscopy. The results are presented together with the analysis of a commercial surface, in order to calculate and compare the absortance and emmittance of the film.

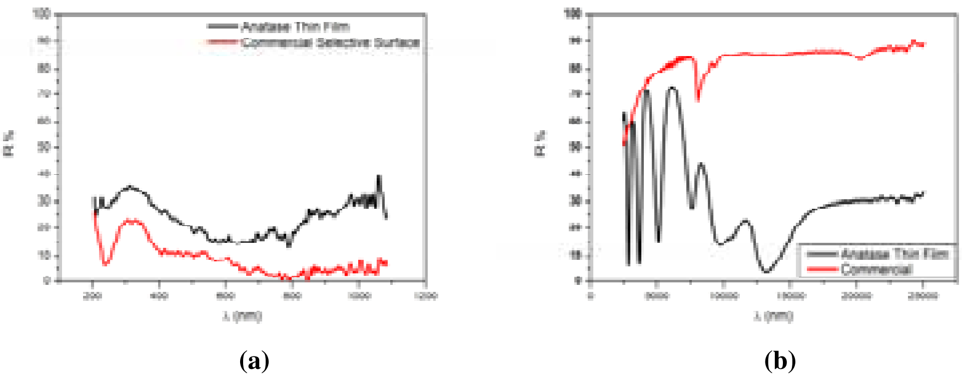


Figure 6. (a) Reflectance curve obtained by UV-Vis and (b) by FTIR for surfaces of anatase and commercial samples.

Solar absortance was measured to be 85% while it was found to be 90% for the analised commercial selective surface. Emittance for the anatase film was approximately 78% while it was 14% for commercial selective surface. The selectivity of anatase films and commercial selective surfaces were 1,10 and 6.43, respectively. A black painted surface was also measured and the achived results were better than the ones observed for this surface as shown in Table 2.

Table 2. Results of optical analysis by UV-Vis and FTIR.

	Anatase Thin Film	Black Painted Surface	Commerical Selective Surface
absortance	85	90	95
emitance	78	14	93
seletivity	1,10	6,43	1,02

5. Conclusions

Anatase thin films were produced on aluminum substrates by electron beam vacuum deposition. The surface of anatase thin films shows nanostructured grains evenly distributed along of all surface. Phase difference image indicates the formation of a nanostructured composite anatase thin film. Chemical analysis by EDX showed that the surface is composed by O, Mn, Mg, Fe, Zn, Zr, Si and Nb. Results of XRD of the surface indicate that the selective surface of anatase grow in an amorphous state. Compositional mapping showed that titanium and iron dominate the surface and are distributed throughout the surface accompanied by silicon, phosphorus and oxygen. Thermal optical results of anatase thin films showed losses of about 78% while black paints have a bigger heat loss in the range of 93%. This result can be optimized by controlling the layer thickness. These results point to the fact that very cheap surfaces, made out of residues of the extrative brasilian industry, can be a good candidate for applications in solar collector, substituting black paintings with advantages.

6. References

Munõz A. G.; Bessone J. B., (2004) Anodic oxide growth on aluminium surfaces modified by cathodic deposition of Ni and Co,**Thin Sol. Films** v.460, 1434.

Chain E. E.; Gesheva K.A.;.Seraphin B.O., (1981) Chemicaly vapor-deposition black molybdenum films of high IR reflectance and significant solar absorptance, **Thin Sol. Films** v.83, 387.

Oelhafen P., A. Schuler A., (2005) Nanostructured materials for solar energy conversion, Solar Energy 79 110-121.

Lampert C. M. (1979) Coatings for enhanced photothermal energy collection I. Selective absorbers, Solar Energy Materials v. 1, issues 5-6.

Tang H., Prasad K., Sanjinbs R., Schmid P. E., and Lévy F., (1993) Ellectrical and optical properties of Ti02 anatase thin films, J. Appl. Phys. 75 (4), 15.

Lima L.C. de ; Macedo M. M. C. ; Albuquerque M. P. ; Albuquerque Marcelo P. And Simão R. A. (2009) Morfological characterization of the surface of nanoporous aluminum oxide by AFM and laws of scale, **NANO**, V.4 N.3 1-8.