www.vbripress.com/aml, DOI: 10.5185/amlett.2016.6623 Published online by the VBRI Press in 2016

Photonic effects on nanostructures in the Ti- TiO_2 interphase

C. P. Barrera-Patiño[1*], Heiddy P. Quiroz[2], R. R. Rey-González[1], A. Dussan[2]

[1]*Grupo de Óptica e Información Cuántico, Departamento de Física, Universidad Nacional de Colombia – Bogotá. Street address: Cra. 30 No. 45-03 Edificio 404 Of. 206 Ciudad Universitaria, 11001, Colombia*
[2]*Grupo de Materiales Nanoestructurados y sus Aplicaciones, Departamento de Física, Universidad Nacional de Colombia – Bogotá. Street address: Cra. 30 No. 45-03 Edificio 404 Lab. 121C Ciudad Universitaria, 11001, Colombia*

[*]Corresponding author. Tel: (+57) 1-3165000; E-mail: cpbarrerap@unal.edu.co

Received: 18 June 2015, Revised: 29 March 2016 and Accepted: 26 May 2016

ABSTRACT

In this work we present a theoretical-experimental study of optics effects in nanostructures formed during the growth of titania nanotubes. Titania nanotubes were fabricated via electrochemical anodization method using Ethylene glycol. Traces or prints left by the nanotubes on the titanium surface are observed thought X-ray diffraction measurements. The pattern shows a polycrystalline structure with the presence of Anatase and titanium phases. The reflectance and absorbance spectra reveal in the traces optical phenomena similar to iridescence. The iridescence behavior is commonly found in nature and is traditionally associated to photonic properties. Using the plane wave method and modelling the nanostructures observed on the interphase like two-dimensional photonic crystals, the photonic dispersion relation was calculated in function of geometrical parameters. Enlargement of the photonic band gap was found as spatial contrast is increased. These results suggest that these types of nanostructures can be promissory candidates to develop photonic devices. Copyright © 2016 VBRI Press.

Keywords: TiO_2 traces; nanotubes; iridescence; photonic.

Introduction

Photonic materials provide the opportunity to control light flux [**1**]. This field has had considerable growth during the last decade. Photonic materials are periodic systems and can be used to develop innovative technological applications [**1, 2**]. In 1979, Ohtaka was the first to introduce photonic terms like photonic band gap and model the propagation of light in periodic systems [**2**]. Also, in 1987, Eli Yablonovitch and Sajeev John simultaneously introduced the term photonic crystal [**3, 4**], both authors proposed a crystalline structure with a range of frequencies in which the propagation of electromagnetic waves is not permitted, this is called photonic band gap. On the other hand, optical properties of titania and titania nanotubes has been studied both theoretically [**5, 6**] and experimentally [**7**] over many years.

In this work, we present an experimental and theoretical study of two-dimensional periodic nanostructures with hexagonal lattice formed during the process of nanotubes fabrication, which is in the titanium-titanium dioxide (Ti-TiO_2) interphase [**8**]. Titania was observed in Anatase phase. The Ti-TiO_2 interphase presents iridescent effects at macroscopic level. This effect might have a connection with photonic properties [**1**].

Experimental

Synthesis of TiO_2 traces

The TiO_2 nanotubes were prepared by Ti thin films anodizing (2 × 4 cm in size, 50 μm thickness, and 99.96% purity) in a solution composed of ethylene glycol, deionized water, and ammonium fluoride (NH_4F). Subsequently two Ti foils working as anode and cathode, separated 2 cm from each other, were introduced in the solution and connected to a DC source by applying a bias current of 80 V for 45 min. Traces were found in the interface of Ti and the TiO_2 nanotubes when these were detached from the titanium foils, a process facilitated by their low adhesion.

Characterizations

These nanostructures were characterized through X-ray diffraction (XRD) measurements using an X Policristal X'Pert Pro (PANalytical) equipped with a Cu-Kα source: 1.540598 Å, 40 kV and 40 mA with a Bragg-Brentano configuration and X'Celerator detector. X'Pert High- Score Plus software was used to compare the samples through Rietveld refined in the range of $10^{º} \leq 2\theta \leq 120^{º}$ with angular steps of 0.02º.

The morphological characterization of the samples, through scanning electron microscopy (SEM) measurements, were performed by using a microscope (VEGA3 SB) with a tungsten filament, an accelerating voltage of 4.89 kV in vacuum conditions (10^{-6} mbar), and XFlash Detector 410M. The optical properties were performed through reflectance spectra obtained using a Cary 5000 spectrophotometer UV-Vis- NIR high yield in the range of 175 to 3300 nm.

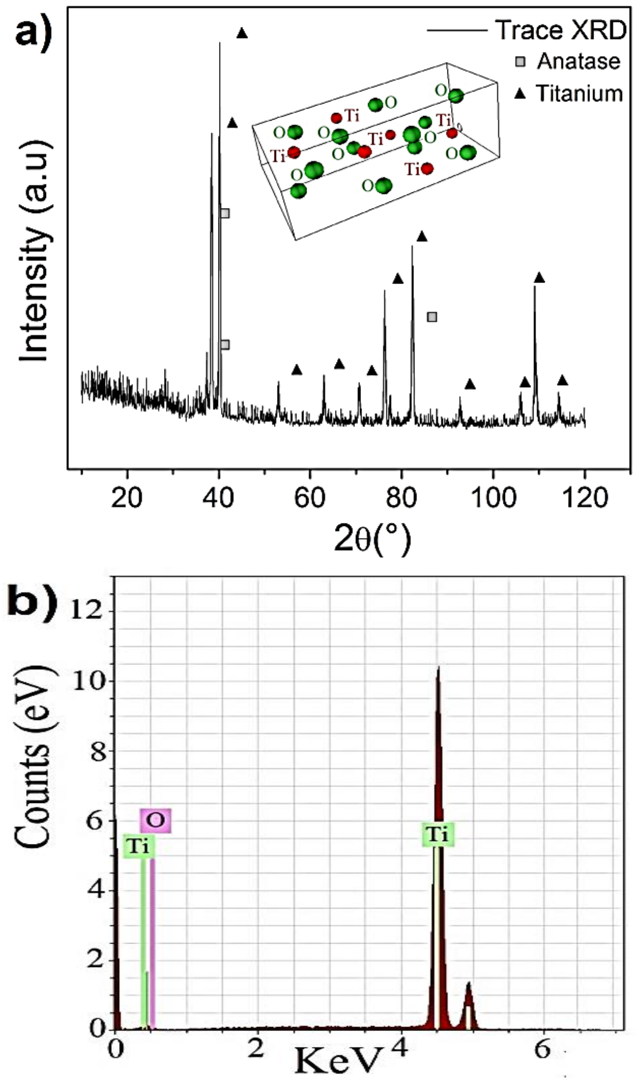

Fig. 1. (**a**) XRD pattern of TiO_2 traces, and (**b**) EDXS superficial analysis of traces.

Theoretical model and computational methods

Photonic crystals have a dielectric nature with periodic modulation of the refractive index. Consequently, the Bloch theorem is valid and these materials must exhibit the formation of photonic bands in analogy to electron bands in crystalline solids [**1**]. The starting point in the analysis of these materials is the second-order equation for the magnetic field:

$$\nabla \times \left[\frac{1}{\varepsilon(r)} \nabla \times \boldsymbol{H}(r)\right] = \left(\frac{\omega(k)}{c}\right)^2 \boldsymbol{H}(r), \qquad (1)$$

Where, k is the wave vector. Taking advantage of crystal periodicity, the plane wave expansion (PWE) method expands in plane wave basis of magnetic field and dielectric function to obtain a finite system of orthogonal integral relationships [**9, 10**]. One important point of band structures calculations is to determine the so-called photonic band gap (PBG), the region where electric or magnetic modes are forbidden. Also, partial PBG exists when electric modes are permitted and magnetic modes are forbidden, and vice-versa. The free MIT Photonics Bands (MPB) [**11**] is an implementation of PWE and it was used to calculate the respective photonic band structure and the PBG.

Results and discussion

Fig. 1 and **Fig. 2a** show the XRD pattern, energy-dispersive X-ray spectroscopy (EDXS) spectra and SEM micrograph obtained from the TiO_2 traces when NH_4F was 0.25 wt% in a constant bias current of 80 V for 45 min. **Fig. 1** shows phases for Anatase at 2θ = 37.34º, 38.31º, 82.62º and Ti at 2θ = 38.46º, 40.18º, and 53.02º.

For peak 2θ = 82.30º a shift towards lower values and the presence of Ti and Anatase phases is observed. The inset in **Fig. 1a** shows the atomic positions in the Anatase phase. Compositional proportions of the elements in the TiO_2 traces were determined by EDXS measurement. It was observed that Ti and oxygen (O) elements are 89.44 ± 2.97 wt% and 10.56 ± 5.40 wt%, respectively.

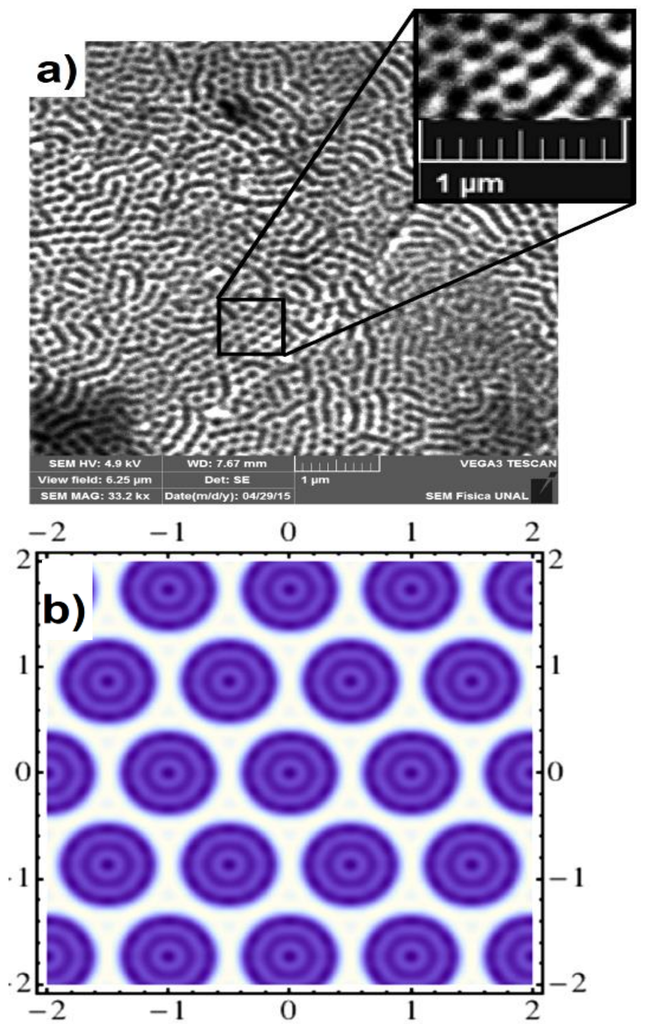

Fig. 2. (**a**) SEM micrograph of TiO_2 traces. (**b**) Schematic representation of the nanostructures (traces) observed in the Ti-TiO_2 interphase.

TiO_2 trace structures are clearly observed over the whole surface. As noted, the traces have a hexagonal shape characterized for thick walls and a diameter around 83.53 ± 1.93 nm. According to the SEM micrograph (**Fig. 2a**), we modeled the nanostructures (traces) at the Ti-TiO_2 interphase as two-dimensional photonic systems formed by a hexagonal array of air columns immersed in a TiO_2 matrix in Anatase phase.

Considering the two-dimensional system in the *xy* plane, using a radii r = 0.42a for air holes and dielectric function of 5.62 [**12**] for Anatase phase, the profile for dielectric function of the traces model was obtained, and is shown in **Fig. 3a**. The photonic band structure for this model does not have a total PBG. A partial PBG for the transverse mode of the electric field of $\Delta\omega = 0.17$ ($\omega a/2\pi c$) wide was found, as observed in **Fig. 3b**.

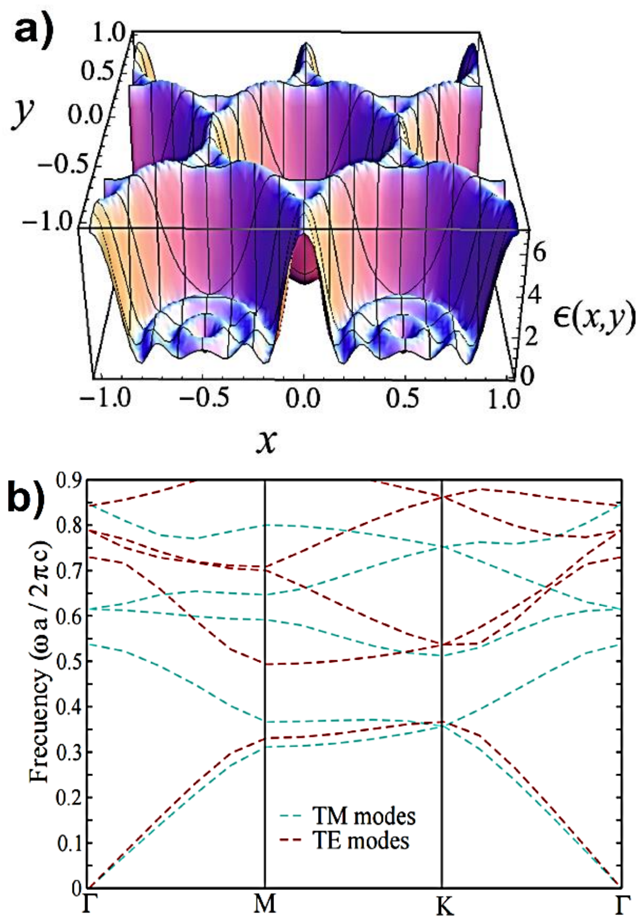

Fig. 3. (a) Profile of dielectric function for the system, and (b) Photonic band structure for the system shown in **Fig. 2b**.

On the other hand, reflectance spectra were obtained for traces and titanium foil samples; this was done by using specular reflectance measurements, varying angle from 20 to 60 degrees (**Fig. 4a**). It was observed that all spectra are characterized for having a reflectance peak around 354 nm in an ultraviolet region followed by an increase of %R before 700 nm. Reflectance peak can be associated to photonic band gap to the transverse electric field for the TiO_2 Anatase phase (**Fig. 3a**, red dashed lines) and a good crystalline quality of the sample (**Fig. 1a**) [**13**]. The photonic band gap is between 0.49 and 0.32 ($\omega a/2\pi c$) on the frequency range. An iridescent effect was observed on samples when the light incidence angle varied from 20 to 60 degrees in specular reflectance. Changes in κ agree with the values obtained from reflectance spectra and absorbance effect inside TiO_2 traces (**Fig. 4b**).

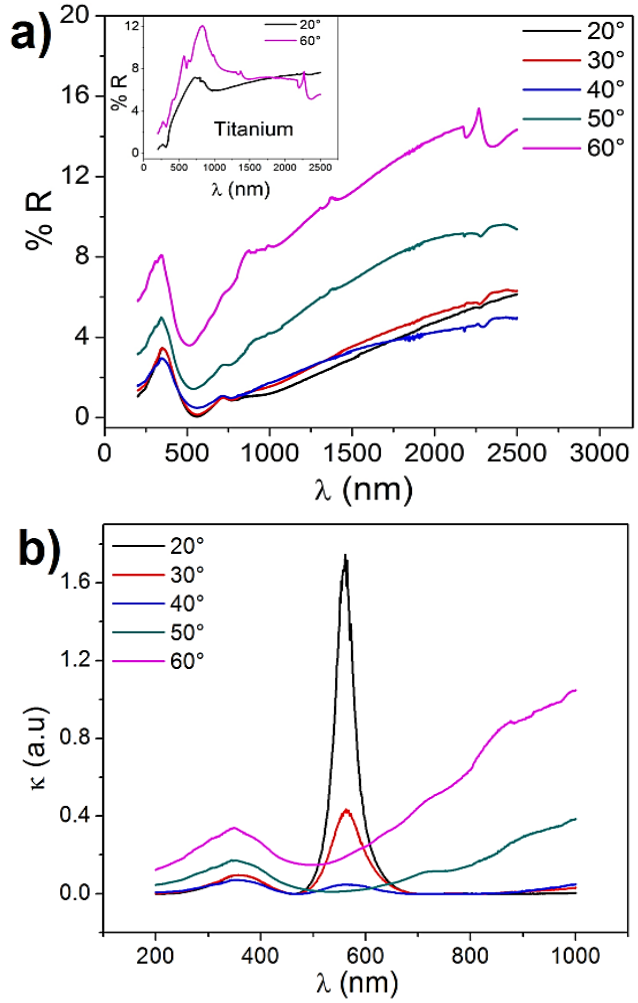

Fig. 4. (a) Reflectance spectra of TiO_2 traces; the inset shows reflectance spectra for two angle values on Ti foil. (b) Extinction coefficient (κ) as a function of λ obtained by reflectance measurements.

Conclusion

Photonic he Anatase phase shows a partial photonic band gap on the electric field for the Ti-TiO_2 interphase. From XRD measurements, the presence of titanium and Anatase phase was observed. Reflectance peaks around 354 nm can be associated to photonic band gap of TiO_2 traces. The extinction coefficient κ obtained showed reflectance and absorbance effects in the sample, evidencing the iridescence phenomena when the angles of specular reflectance varied between 20 and 60 degrees.

Acknowledgements

This work was supported by Universidad Nacional de Colombia and DIB, Project Cod. Quipú No. 201010020493 and Colciencias Project Cod. Quipú No. 201010019609.

References

1. Joannopoulos, J. D.; Johnson, S. G.; Winn, J. N.; Meade, R. D. Photonic Crystals Molding the Flow of Light; Princeton University Press: New Jersey, 2008, pp. 1-17.
2. Ohtaka, K.; *Phys. Rev. B*, **1979**, *19*, 5057. **DOI:** 10.1103/PhysRevB.19.5057
3. Yablonovitch, E.; *Phys. Rev. Lett.*, **1987**, *58*, 2059. **DOI:** 10.1103/PhysRevLett.58.2059
4. John, S.; *Phys. Rev. Lett.*, **1987**, *58*, 2486. **DOI:** 10.1103/PhysRevLett.58.2486

5. Radhakrishnan, T.; *Proc. Indian Acad. Sci. Sect A*, **1951**, *33*, 22.
6. Glassford, K. M.; Chelikowsky, J. R.; *Phys. Rev. B*, **1992**, *45*, 3874.
   DOI: 10.1103/PhysRevB.45.3874
7. Hossain, F. M.; Evteev, A. V.; Belova, I. V.; Nowotny, J. ; Murch, G. E.; *Adv. Appl. Ceram.*, **2012**, *111*, 72.
   DOI: 10.1179/1743676111Y.0000000063
8. Dussan, A.; Quiroz, H.P; *Adv. Mater. Res.*, **2015**, *1119*, 121.
   DOI: 10.4028/www.scientific.net/AMR.1119.121
9. Ho, K. M.; Chan, C. T.; Soukoulis, C. M.; *Phys. Rev. Lett.*, **1990**, *65*, 3152.
   DOI: 10.1103/PhysRevLett.65.3152
10. Johnson, S. G.; Joannopoulos, J. D.; *Opt. Express*, **2001**, *8*, 173.
   DOI: 10.1364/OE.8.000173
11. http://abinitio.mit.edu/wiki/index.php/MIT_Photonic_Bands, **2015** (Packet MIT).
12. Mo, S. D.; Ching, W. Y.; *Phys. Rev. B*, **1995**, *51*, 13023.
   DOI: 10.1103/PhysRevB.51.13023
13. Palacios-Lidón, E.; Blanco, A.; Ibisate, M.; Meseguer, F.; López, C.; *Appl. Phys. Lett.*, **2002**, *81*, 4925.
   DOI: 10.1063/1.1530752

