Photocatalytic activity of coatings based on titanium oxides deposited by reactive magnetron sputtering method

Actividad fotocatalítica de recubrimientos de óxidos de titanio depositados por pulverización catódica reactiva

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Palabras clave

Óxidos de Titanio; Foto catalítico; Capas Delgadas; Deposición; Pulverización Catódica.

Resumen

El objetivo de este proyecto es medir la actividad fotocatalitica de capas delgadas de óxidos de Titanio depositadas por Pulverización Catódica con Magnetrón. Los recubrimientos se depositaron en sustratos de silicón utilizando una mezcla de gases Ar – O^2 y titanio puro como target. Como resultados, se obtuvo una composición química de $Ti1-_xO_x$ donde x varía de 2,25 a 0,45. De acuerdo a los resultados de las pruebas de Adhesión, la carga mínima obtenida fue de 14,43 N mientras que la mayor fue de 72,01 N. Los resultados de las pruebas para la actividad fotocatalítica mostraron que las muestras no eran reactivas ya que no se obtuvo un cambio de color en el ácido naranja, sustancia en la cual fueron sumergidas, luego de que las muestras estuvieran expuestas a la luz ultravioleta.

Keywords

Titanium Oxides; Photocatalytic; Thin Film; Deposition; Sputtering Magnetron.

Abstract

The aim of this project is to measure the photocatalytic activity of titanium oxides thin layers deposited by reactive magnetron sputtering method. The coatings were deposited onto silicon substrates in gas misxture of Ar and O^2 and as target was used pure titanium. Chemical composition of coatings was varied by change of O^2 flow. As results, it was obtained a chemical composition $Ti1-_xO_x$ where x is from 0,25 to 0,45. According to the adhesion scratch test, the lowest critical load was 14,43 N and highest was 72,01 N. Results from photocatalytic activity indicates that the samples were not active due to the acid orange in which they were submerge presented no change of color after the UV light exposition.

Introducción

Thins films are known as layers of material which are deposited on a substrate with a thickness measured in nanometers in order to improve or modify the properties of the substrate. Nowadays the fabrication of thin layer has become more important due to its various applications such as electronics, coatings, optical application among others. These types of layers can be made using different processes such as Magnetron Sputtering. This method is a form of Physical Vapor Deposition technology and consists in a plasma coating process whereby sputtering material is ejected due to bombardment ions to the target surface. By applying a high voltage, a glow discharge is created, resulting in acceleration of ions to the target surface and a plasma coating [2]. Magnetron sputtering technology is characterized by:

- Almost any metallic target material can be sputtered without decomposition
- Oxide coating can be sputtered
- No droplets are generated; very smooth sputtered coatings are created.
- Nonconductive materials can be sputtered by using radio frequency (RF) or medium frequency (MF) power.

Thin films are characterized by some important properties that will define if the process preparation was successful and if the thin layer has a good quality. Some of those properties are:

- Thickness: can affect the structure, surface and other properties of the thin, so it's important to know it value in order to understand the surface behavior.
- Adhesion: the importance of measuring the adhesion of the thin layer relies on knowing how well the thin film adheres to the substrate.
- Friction and Wear: friction is defined as the result of the quality of relative motion between two surfaces meanwhile the wear of a thin layer is the surface damage process.

There are many materials of which thin layers can be made but nowadays many researches are focus on Titanium Dioxide (TiO^2) due to its variety of application such as self-cleaning surfaces, water purifications systems and photoelectrochemical conversion but besides all those applications, TiO^2 is now known because of its good ability on photocatalysis. The high photocatalytic activity of TiO^2 is primarily due to the large ban gap between the valence and conduction bands, resulting in high redox power [1].

Experimental Details

Substrate Preparation and Titanium Oxide Coating

The experiment was made three times in which a set of five silicon samples were prepared per experiment.

All samples were cleaned using acetone and an ultrasonic cleaning surface (Novatec Surface Finishing) after that all samples were dry by air.

Once the cleaning process was finished, the coating process was made by magnetron sputtering using the Hauzer Flexicoat 850. All the samples were coated using a pure titanium target and Ar and O^2 gas flows.

Table 1. Gas Flow Rates for the Experiments.

Sample	Ar (sccm)	O^2 (sccm)	
		Start	End
1	95	10	40
2	95	20	65
3	95	10	65

Chemical Composition

The chemical composition was varied by change on the O^2 gas flow, as it can be seeing in table 1. Samples were analyzed using the JSM-7600F Scanning Electron Microscope.

Thin Layer Properties

The properties measured in this experiment were adhesion which was examined with the Revestest Scratch Testing and thickness measured using Calotest CSM Instrument. Also a Rockwell Adhesion Test was performed on sample 2.

Photocatalytic Activity

The photocatalytic activity was measured using the machine shown in figure 1. For the experiment the acid orange 7 (20 μmol/l) was used as the substance were the samples will be immerse. For each sample a volume of 25 ± 0.40 ml, was used. After the preparation, samples were put under the UV light for five hours.

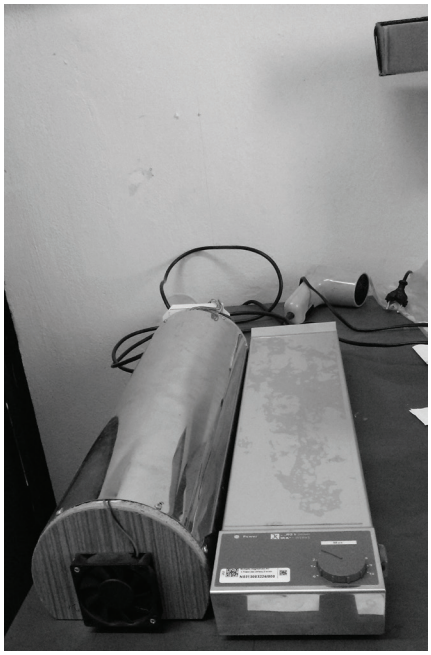

Figure 1. Equipment for Photocatalytic Activity Measurement.

Results and Discussion

Chemical Composition

The results for the three samples are shown on table 2. SEM results showed that the first sample had a metallic composition due to its majority part were Titanium with 78,65%. For the second experiment, which had a bigger amount of oxygen than the first one, a composition of 58,36% of Ti was obtained which indicates that the oxide was create but the sample wasn't stoichiometric correct yet.

In the case of the third experiment the oxide was created with a composition of 54,85% of Ti and 2,93% of O indicating that the sample was stoichiometric correct.

Table 2. Chemical Composition (Weight %) obtained by SEM.

Element	Sample 1	Sample 2	Sample 3
Ti	78,65	58,36	54,85
O	21,19	41,64	2,93
Si	0,16	-	0,8
Ar	-	-	41,45
Total	100	100	100

In figure 2, the surface of samples 2 and 3 obtained from SEM analyzes can be seeing. In the images a homogenous surface can be observed with white dots which represent a little amount of nitrogen that was leaking from the chamber at the moment the experiment was made.

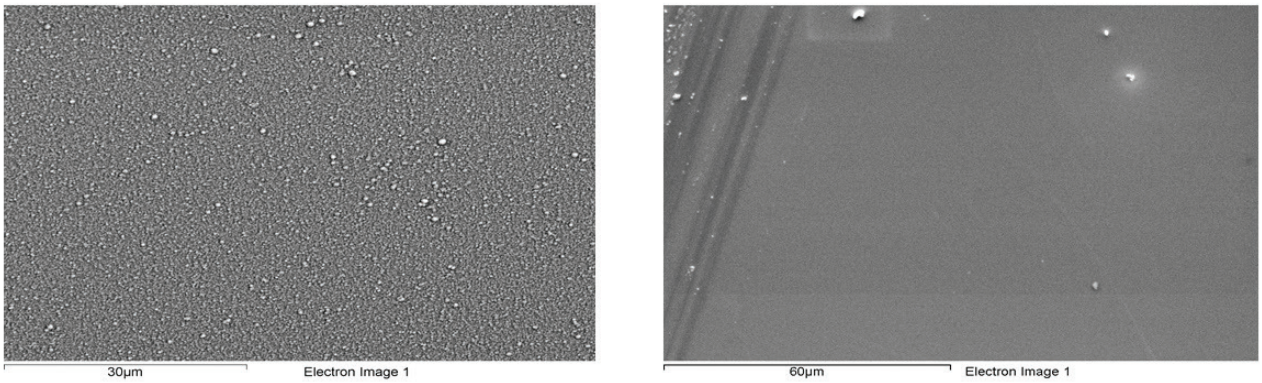

Figure 2. Surface Image obtained by SEM: a) Sample 2 at a scale of 30 m b) Sample 3 at a scale of 60 µm.

Thickness

Calotest results showed that sample 1 obtained a thickness of 1 µm, being the thinner one of the three samples. Coating 2 was the thicker one with 1,72 µm and in the case of Sample 30,72 µm of thickness was measured.

Rockwell Adhesion Test

The Rockwell Adhesion Test was performed only on a steel sample from the second try. In Figure 3, according to the DB Adhesion Classification (figure 4), the sample showed an acceptable adhesion which indicates that the layer was correctly adhered to the substrate.

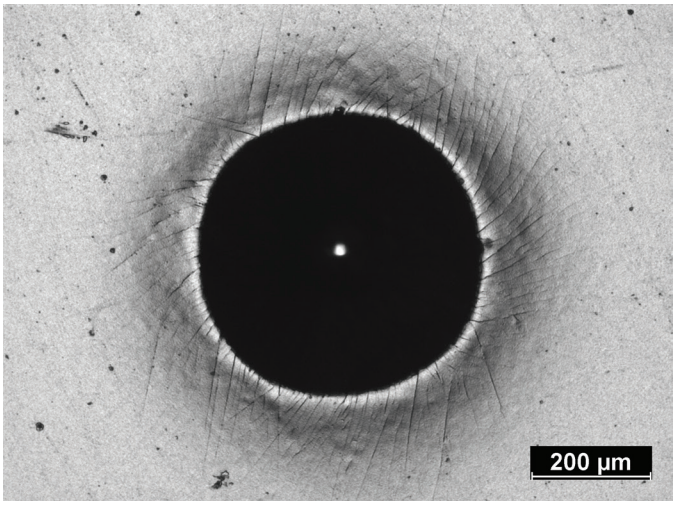

Figure 3. Rockwell Adhesion Test for the steel sample of the second try.

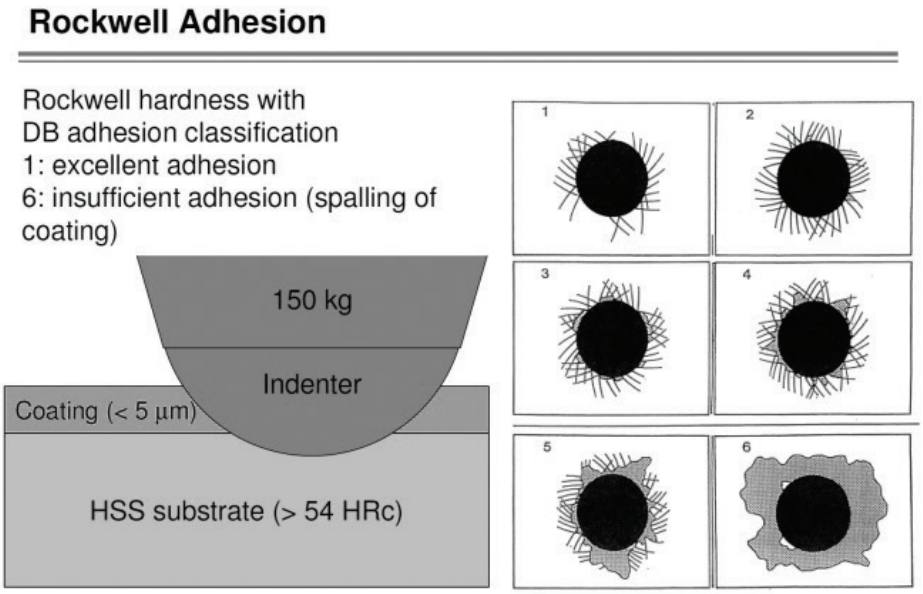

Figure 4. Rockwell Adhesion Classification.

Adhesion Scratch Test

According to figure 5 it can be seeing that the first crack of the sample was showed at 38,75 N, defining this load as the Critical Load of Sample 1. In Sample 2, figure 6 showed the behavior of the sample under loads from 34,82 N and 52,15 N.

Sample 3 showed a critical load of 14,43 N and after 27,15 N bigger crackers can be observed in the sample (figure 7), being this sample the one with lowest loads of the three.

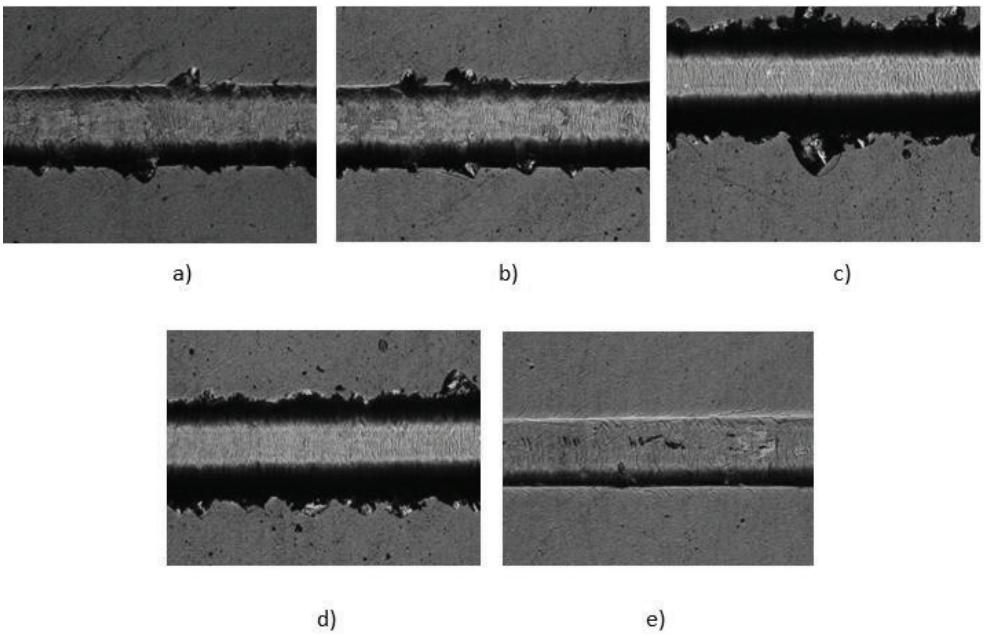

Figure 5. Scratch Test for Sample 1: a) 38,75 N b) 42,96 N c) 62,54 N d) 56, 08 N e) 30,66 N.

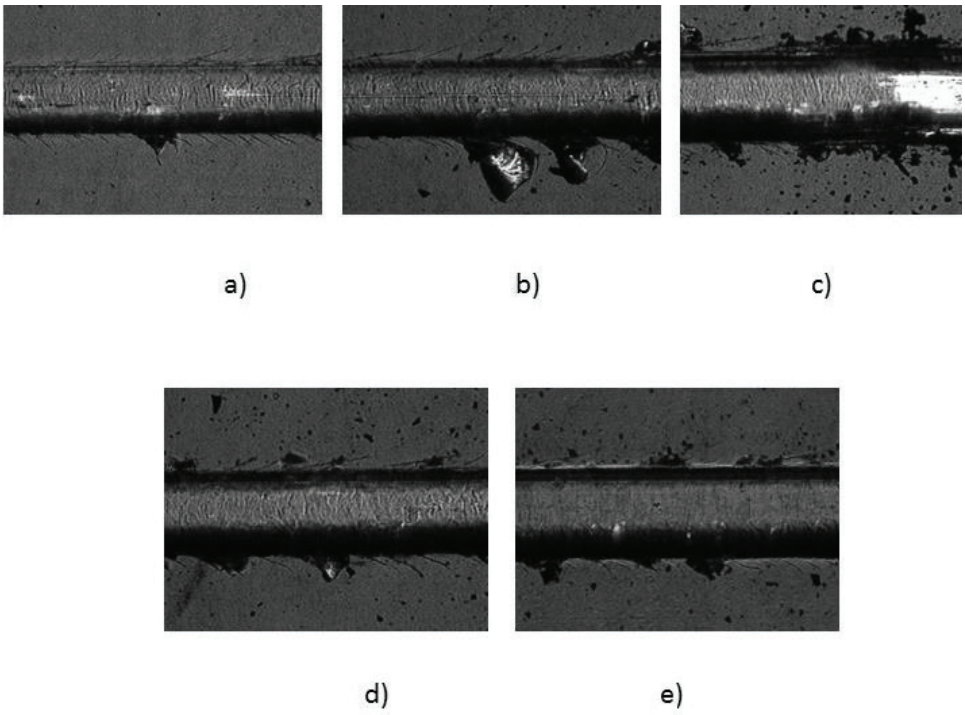

Figure 6. Scratch Test for Sample 2: a) 34,82 N b) 40,89 N c) 58,54 N d) 47,53 N e) 52,15 N.

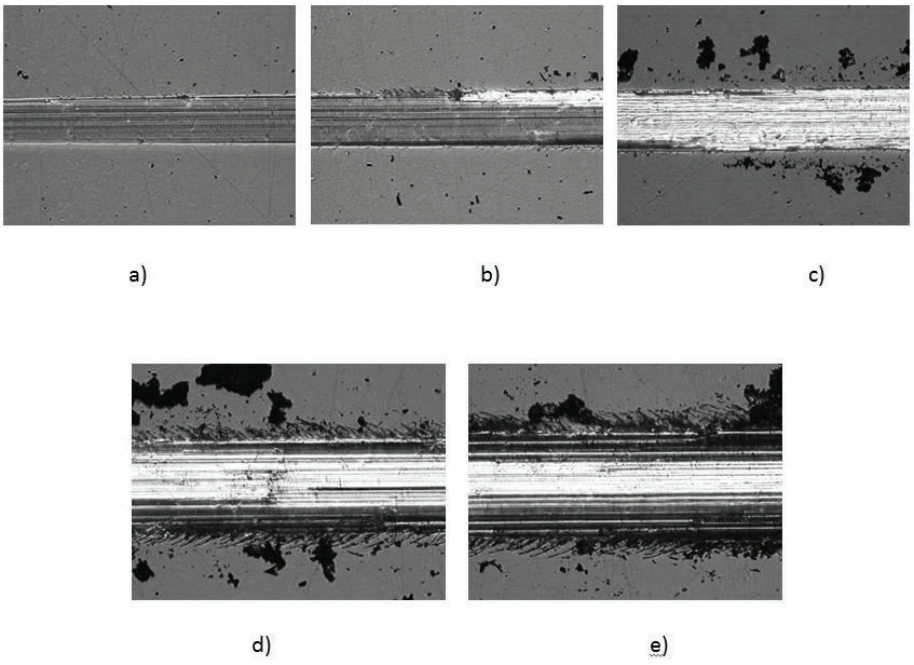

Figure 7. Scratch Test for Sample 3: a) 14,43 N b) 20,83 N c) 27,18 N d) 55,68 N e) 72,01 N.

Photocatalytic Activity

After taking the samples out from the UV light, the acid orange showed no change of color indicating that the samples were not active.

It was expected that the samples were not active due to the absence of previous testing that could orient on an effective way the samples preparation.

Conclusions

Once the experiment was finished, it can be concluded that using a rate of 95 sccm Ar and Oxygen from 10 to 65 sccm an stoichiometric oxide can be created with a composition of 41,45% O and 54,85 Ti. On the other hand, with lower amounts of oxygen a composition of $Ti1-_xO_x$ was obtained in where x goes from 0,25 to 0,45.

According to the measured properties, in the adhesion scratch test the lowest critical load obtained was 14,43 N meanwhile the highest one was 72,01 N, both from Sample 3.

For the photocatalytic activity none of the samples were active however this result was expected due to the absence of previous testing in the laboratories that could orient on an effective way the samples preparation.

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