TiO$_2$ Synthesis Anatase Phase with The Sol-gel Process at Room Temperature

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Abstract. Titanium oxide (TiO$_2$) film was deposited on 304 stainless steel substrates using the spin coating technique. The synthesis of the deposited solution was with the sol-gel method at room temperature, using titanium isopropoxide as a precursor. Obtained film was thermally treated at temperatures of 500 ºC, 550 ºC and 600 ºC. The X-ray diffraction (XRD) analysis confirmed the crystallinity of the film in the anatase phase, with the highest intensity at the plane (101). Moreover, the crystallite size increased with the rising temperature of the thermal treatment. The thickness of the deposited film was obtained with profilometry being: 1 µm for the 500 ºC film, 1.2 µm for the 550 ºC film, and 1.5 µm for the 600 ºC film. Raman spectroscopy measurements showed vibrational modes at 144, 399, 519 and 638 cm$^{-1}$, characteristic of the TiO$_2$ anatase phase. The obtained results showed that these films have a high potential for gas sensor applications due to their surface-to-volume ratio after obtaining the size of nanometric crystallite.

1. Introduction

Respiratory illnesses in the last few years have increased due to volatile organic compound (VOC) emissions [1]. Certain VOCs have pleasant odors or are odorless, making them difficult to detect. They can cause poisoning and cancer, therefore a gas sensor which can detect human physical integrity is necessary. There are different gas sensors which are covered with titanium oxide (TiO$_2$) nanostructured film with its oxygen vacancy mechanism (redox), as well as its ionization mechanism [2-4]. TiO$_2$ is a type n semiconductor with a bandwidth prohibited from 3 to 3.6 eV. TiO$_2$ is not toxic, can be used in hostile environments, and has three crystalline phases: anatase, rutile (both tetragonal), and brookite (orthorhombic). The anatase crystalline structure is the most commonly used for gas sensors because of its greater reactivity and simple crystalizing structure, starting at 400 ºC [5]. TiO$_2$ can be obtained with different methods, the most utilized being chemical vapor deposition (CVD), precipitation, sputtering, and sol-gel [4, 5, 7]. The sol-gel method is a chemical synthesis that offers great benefits compared to other techniques. It has a low cost, good homogeneity, film thickness control, room temperature deposits,
and porous film. The most commonly used precursor for film formation is a metallic alkoxide dissolved in hydrolyzed alcohol in an acidic, neutral, or basic environment [7,8]. TiO$_2$ film properties deposited with spin coating can vary, depending on centrifuge velocity, time, and the evaporation of the solution. Moreover, it can be deposited on different substrates such as glass, silicon, and 304 stainless steel [7,9,10]. 304 stainless steel was selected for this study due to its good properties for the implementation of oscillate structures. 304 stainless steel can withstand thermal treatments of up to 900 °C, has an accessible price, and mechanical properties similar to silicon, which is why it is used as a substrate for gas sensors. The synthesis and the results of multilayer TiO$_2$ film deposited in 304 stainless steel substrates with the spin coating method annealed at different temperatures are presented in the following sections.

2. Methodology
TiO$_2$ was synthesized using titanium isopropoxide (TTIP) as a precursor with an ethanol concentration of 0.0025 M. Hydrochloric acid (HCl) was added at a concentration of 0.0014 M. This mix was maintained in continuous agitation at room temperature for 10 minutes until a transparent and homogeneous solution was obtained. The obtained solution was deposited on 304 stainless steel substrates in an area of 2 cm by 2 cm with spin coating at 2000 revolutions per minute (rpm) for 17 seconds at room temperature. The deposited film dried at 200 °C for 5 minutes to eliminate organic solvent, and this deposit-drying process was repeated 10 times. Finally, the dry film was annealed at 500 °C, 550 °C, and 600 °C for 2 hours. The obtained film was analyzed by means of X-ray diffraction with the Bruker D8 Advance, with CuKα radiation. The vibrational modes of TiO$_2$ film were obtained with Raman spectroscopy using a 623.8 nm Neon (He-Ne) helium laser. The profilometry measurements were taken with a Veeco Dettak 150 profilometer, which scanned with a micro-point 3 mm above the surface.

3. Results and discussion
The TiO$_2$ film deposited on the 304 stainless steel substrates with thermal treatments of 500 °C, 550 °C, and 600 °C had excellent uniformity and qualitative adherence. Figure 1 shows the X-ray diffraction results for the TiO$_2$ film on 304 stainless steel substrates with a variation of thermal treatments at 500 °C, 550 °C, and 600 °C, showing tetragonal anatase phase, which conforms to PDF #01-072-7058. All the diffractograms show the film have the most intensity at the plane (101). As the temperature at the crystalline plane increases, a slight shift in tension can be seen.

Crystal size was theoretically calculated with the Scherrer equation by using the peak (101) [11]:

$$L = \frac{k \lambda}{\beta \cos \theta}$$  (1)

The crystallite size for the 500 °C TiO$_2$ sample is 24.7 nm, the 550 °C TiO$_2$ sample is 25.4 nm, and the 600 °C TiO$_2$ sample is 26.6 nm. The nanometric crystallite size allows us to apply this film to objects such as gas sensors, due to the strong interaction between the TiO$_2$ nanoparticles and the gas to be detected and the surface-to-volume ratio between them. Film thickness was obtained with profilometry measurements, giving us the following results: 1 µm, 1.2 µm and 1.5 µm for the annealed film at temperatures of 500 °C, 550 °C and 600 °C respectively.

The tension shifts were analyzed with the Stoney equation [12] for TiO$_2$ film with thermic treatments of 550 °C and 600 °C at 2 theta (2θ), the shifts were found at 25.20 and 25.19 °.

$$\sigma_s = -\frac{E}{\mu} \frac{d - d_0}{d_0}$$  (2)

Location: E is the Young module (151 Gpa), $\mu$ is the TiO$_2$ Poisson coefficient (0.27) [13], $d_0$ is the tension-free network reference (3.518310 Å), conforming to the PDF #01-072-7058 document, and $d$ is the interplanar sample distance to be analyzed. The results were 2.26 GPa for 550 °C and 2.04 GPa for 600 °C.
Figure 1. X-ray diffractograms of TiO₂ anatase phase film with thermal treatments of 500 °C, 550 °C and 600 °C.

Figure 2 shows Raman spectrums for the deposited film treated at different temperatures. These spectrums have vibrational modes of Eg (144 cm⁻¹ and 638 cm⁻¹), B₁g (399 cm⁻¹ and 519 cm⁻¹), and A₁g (519 cm⁻¹), confirming the presence of TiO₂ anatase phase [10]. This reveals a compression shift and better crystallinity at vibrational mode Eg (144 cm⁻¹), which is associated with a particle size of less than 40 nm, matching the grain size calculated from the TiO₂ film [14].

Figure 2. Raman spectrum of TiO₂ anatase phase multilayer film with thermal treatments of 500 °C, 550 °C and 600 °C.
4. Conclusions
A TiO$_2$ solution was synthesized using the sol-gel route at room temperature. The TiO$_2$ solution was deposited on 304 stainless steel substrates with high homogeneity and good adherence on the substrate. The obtained X-ray diffraction and Raman spectroscopy results confirm the presence of TiO$_2$ at the anatase phase with a preferential growth at the plane (101). The crystallinity of the TiO$_2$ film varied in function with the temperature. The deposited film in this study has a high potential to be used for gas sensors due to the preferential growth at the plane (101) and the presence of the tetragonal anatase phase. The nanometric crystallite size allows for better interaction between the TiO$_2$ film and the gas to be detected with there is a greater contact surface area.

As future work, studies of characterization as photoluminescence, nanoindentation, and performance of the multilayer TiO$_2$ films will be realized in a gas chamber with different VOCs.

5. References
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Acknowledgments
This research was funded by project PRODEP “Modelado y Desarrollo de Microsensores CMOS-MEMS para la detección de diabetes” and CONACYT trough Grant 517529 by Program of Doctorate in Materials and Nanoscience of the Research Center in Micro and Nanotechnology of University of Veracruz (MICRONA-UV), México.