Influence of Substrate Temperatures on Morphological TiO₂ Nano-layers Properties

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Abstract

This paper presents the elaboration of titanium dioxide TiO₂ nano-layers for different temperatures. The nano-layers are deposited by radio frequency (RF) magnetron sputtering technique. In this work the analyzed of temperature effect on the optical and surface condition properties are investigated using Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDS), Atomic Force Microscopy (AFM) and UV–visible spectroscopy. The TiO₂ nano-layers surface roughness range from 1.04 nm to 1.6 nm for 450°C and 300°C, respectively. UV–visible spectrophotometry characterization of the deposited TiO₂ nano-layers show that the films gap varies according to the temperature variation with 3,6eV for T=300 and 3.8eV for T=450°C. We can deduce that the optical gap varies proportionally with the temperature variation. Otherwise, the EDS results imply the formation of TiO₂.

Keywords
 Semiconductor, TiO₂ nano-films, magnetron sputtering, AFM, SEM, EDS.

1. Introduction

Nowadays, semiconductor materials are widely studied and adapted to various applications for their electrical, catalytic and optical excellent properties. In comparison with other semiconductor, titanium dioxide (TiO₂) has been the subject of immense researches for its nontoxic nature, unique optical and electrical properties, high chemical stability and stable against corrosion (Ghrairi and Bouaicha 2012), (Mengjin 2012), (Zhen et al. 2008), (Bedoud et al. 2019), (Manouchehri et al. 2016), (Kuo et al. 2012), (Twu et al. 2015). TiO₂ thin film is highly transparent in visible and infrared spectral range and absorbent in UV region. So, it has a high refractive index n and wide optical band gap. Titanium dioxide can exist in three distinct crystalline phases : anatase, brookite and rutile phases (Golubović et al. 2009). TiO₂ is widely used in various applications such as: electronics, photonics, sensing, medicine, and controlled drug release. Titanium oxide is used also in various fields such as solar cells, optical coatings and widely used in memory devices (Kondaiah et al. 2012). However, only anatase and rutile structures are commonly observed in thin film form (Kondaiah et al. 2012), (Nair et al. 2011). The TiO₂ nano-layers can be synthesized using various techniques (Hassan et al. 2019), (Chen et al. 2018), (Tbessi et al. 2019), (Tehe Ky et al. 2018): pulsed laser deposition, sputtering, sol–gel and spray pyrolysis. So, among these methods, RF-DC magnetron sputtering is widely used due to its several advantages. The authors in (Bukauskas et al. 2015) have studied the substrate temperature effect on the characteristics of ultra-thin TiO₂ films. For this the substrate was kept at diverse temperatures during both and post deposition. As it was demonstrated, the formation of the ultra-thin TiO₂ films during sputtering can be modified significantly by changing the substrate temperature. In a work by (Abreu et al. 2015), the evaluation of the tribological properties of TiO₂/Au by PVD magnetron sputtering technology was investigated. So, Thermal annealing at higher temperature had detrimental effect on the tribological properties of the films due to important structural changes as increasing of crystallinity and nanoparticle gain size. In (Yang et al. 2008), authors have presented a work on the study of the temperature effects on Ti thin films optical properties, where they determined optical parameters (optical band gap energy, conductivity, dielectric constants and dissipation factor). They conclude that, with increasing deposition time, surface roughness increases. Optical measurements indicate that transmittance decreases with increasing sputtering time in visible and infrared spectral range. Preliminary results on the morphological study of nano-films made on glass substrates are presented and discussed. Otherwise, the detection and identification of CO₂ level in closed spaces are
very important spots and even necessary. Indeed, during the last few years, gas sensors based on semiconducting oxide nanostructures have been widely investigated.

The study presented in this paper consists of the high-quality TiO₂ nano-films deposition by magnetron sputtering and investigating the temperature effect on the morphological properties for gas sensor development.

2. Experimental Part

The TiO₂ nano-layers were elaborated under RF mode of magnetron sputtering system. The substrate was rated at 20rpm and the distance between the substrate and target was fixed at 11cm. In order to remove impurities in the void, the sputtering chamber was pre-sputtered at a base pressure of 10⁻⁴ Torr for 45mn. The gas used are pure argon as the sputtering gas and pure oxygen as the reactive gas. Table 1 summarized the operating mode.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>E01</th>
<th>E02</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF : Power (≤ 300)</td>
<td>150W</td>
<td>150W</td>
</tr>
<tr>
<td>Argon flow (sccm)</td>
<td>60sccm</td>
<td>10sccm</td>
</tr>
<tr>
<td>Oxygen flow (sccm)</td>
<td>10sccm</td>
<td>50sccm</td>
</tr>
<tr>
<td>Deposition time (min)</td>
<td>120mn</td>
<td>45mn</td>
</tr>
</tbody>
</table>

2.1 Atomic Force Microscopy Surface Condition Study

Surface morphological investigation of TiO₂ films was examined by atomic force microscopy (AFM) model MFD-3D classic Asylum research (URME-Univ-Setif 1). Figure 1 shows the TiO₂ nano-layers AFM image for T=300°C. We can note that the TiO₂ nano-layers surface roughness is 1.6 nm. Furthermore, from TiO₂ nano-layers AFM image for T=450°C presented in figure 2 the surface roughness is 1.04 nm. Indeed, a smoothest surface is observed for T=450°C.

![Figure 1. 3D AFM images (10x10 nm) of the as sputtered TiO₂ thin films for T=300°C](image-url)
2.2 Study of Surface Condition by Scanning Electron Microscopy (SEM)

In this session, the SEM micrographs for surface morphologies of TiO\textsubscript{2} nano-films are presented. Figure 3 (a and b) indicate different magnification SEM images of nano-film at T=300°C. Simultaneously, Figure 4(a and b) show various magnification SEM of those deposited at T=450°C. The mean particle size values of TiO\textsubscript{2} nano-film is 54 nm for 300°C and 450°C, respectively. The surface of the film is flat and the size of grain on the surface is even. We can observed the decrease in the particle size with the increase of temperature. Therefore, the atoms of the films get sufficient energy to diffuse on the substrate and form a flat surface without holes depending on the elaboration temperature (R. Ananthakumar et al. 2012).

Figure 3. SEM Images of TiO\textsubscript{2} thin films annealed at 300°C
2.3 Energy dispersive study (EDS)

Energy dispersive analysis (EDS) is based on the principle of electron-matter interactions. The observations and microanalyses were carried out with a scanning microscope of the ZEISS Gemini SEM 300 brand. For EDS analyzes, the ray counting speed was estimated at 2x100 counts/s. The mass percentages of each element from the spectra are obtained using the "ZAF" correction method. Figure 5 show the microanalysis EDS for T=300°C. We can note the coexistence of Ti and O in the same place (k). This, gives evidence of the formation of the stoichiometric compound. Furthermore, the EDS pattern of TiO$_2$ films shows that the titanium and oxygen average atomic percentage is equal to 15.17% and 84.83% for T=300°C, respectively. On the other hand, for T = 450 °C as shown in figure 6, we found that the percentages vary, where the oxygen level is 18.23%, and that of titanium has reached 81.77%, which reveals the thin films are oxygen excess due to the presence of oxygen in the deposited TiO$_2$ films. The EDS results are summarized in Table 2.
2.4 Transmittance spectra study

The optical transmitance spectra were measured using Jasco V-760 spectro-photometer covering the UV-visible range with scan speed 300nm/min corresponding to the wavelength range: 190-900nm at room temperature. From the transmittance spectra, it is possible to calculate the energy value of semiconductor forbidden band from Tauc formula (\(E_g\) (eV)) defined by the following equation (Manouchehri et al. 2016), (Bedoud et al. 2019):

\[
(\alpha h\nu)^{1/2} = A(h\nu - E_g)
\]
\[
\alpha = \frac{A}{d} T
\]

The incident photons energy \((h\nu)\) can be calculated as follows:

\[
h\nu = \frac{1240}{\lambda}
\]

Where:
- \(\alpha\) (cm\(^{-1}\)) : optical absorption coefficient;
- \(A\) : constant;
- \(d\):0.5-0.6mm sample thickness (1mm);
- \(E_g\) (eV) : optical gap energy;
- \(h\nu\) (eV) : incident photon energy;
- \(T\) : transmittance spectra.

Figure 7 presents band gaps of TiO\(_2\) films. The films gap varies according to the temperature variation with 3.6eV and 3.8eV for \(T=300\) and \(T=450\)°C, respectively. Therefore, when the temperature increases the optical gap also increases. These results can be compared with those established by: (Yang et al. 2008), (Ananthakumar et al. 2012), (M.R. Teresa et all) and (Viseu and M. Ferreira 1999). However, as we know, the band gap variation is in agreement with changes of crystallographic structures. In semiconductors optical band gap changes with temperatures lightly. We know that increasing temperature expands crystal volume and hence lattice constant so in return it affects bond structure which is a sensitive function of lattice parameter (Manouchehri et al. 2016). The variation in the gap is caused by the Burstein-
Moss effect. The blue shift at the beginning of TiO₂ layer absorption is related to the increase in the concentration of charge carriers blocking the lowest states of the conduction band.

3. Conclusion
In this paper, the growth of the titanium nano-layers using a ceramic Ti target was presented. This study aims to examine TiO₂ nano-films morphology for two temperature. Surface morphology was characterized. Following AFM characterization results, it is found that a smoothest surface is observed for T=450°C. In addition, we can note the coexistence of Ti and O in the same place (k) from the microanalysis EDS. This, gives evidence of the formation of the stoichiometric compound, and reveal that the films are oxygen excess. However, optical measurements indicate that the gap decreases with increasing temperature in visible and infrared spectral range. For the rest of this work, we plan to study the variation of the deposited nano-layers thickness and the elaboration conditions such as: the pressure, the sputtering and reactive gases flux on the morphological, optical and electrical TiO₂ Nano-layers characteristics.

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