Preparation and Characterization of (TiO$_2$-SnO$_2$) Thin Films by Pulsed Laser Deposition

Saja H. Rashed  
Science College, Baghdad University/Baghdad  
Email: sajahatem90@yahoo.com 
Dr. Adawiyah J. Haider  
Applied Sciences Department, University of Technology/ Baghdad  
Email: Adawiyahaider@yahoo.com 
Dr. Samar Younis  
Science College, Baghdad University/Baghdad

ABSTRACT

In this work, mixed oxide (TiO$_2$-SnO$_2$) thin films were grown on Si (111) and glass substrates by pulsed laser deposition (PLD) method. The influences of increasing amounts of SnO$_2$ were investigated. The X-ray diffraction results show the peaks position of the plane was shifted towards higher angle values with increasing amounts of SnO$_2$. The surface morphology of the deposits materials was also studied by using a scanning electron microscope (SEM). The results show that, the grain sizes decreases with increasing SnO$_2$ content from the largest value (53.6) nm to smallest value (25.5) nm. From UV-visible spectroscopy, the distinct variations in the transmission spectra, and optical energy gap, of the thin films were also observed.

Keywords: Pulsed Laser Deposition (PLD), (TiO$_2$-SnO$_2$) Thin Films, Structural Properties, Surface Morphology, Optical Properties

يتضمن هذا العمل ترسيب غشاء مكون من خليط أوكسيد التيتانيوم وأوكسيد السيليكون والزجاج باستخدام طريقة الترسيب بالليزر النبضي وقد تم مناقشة تأثير زيادة نسبة أوكسيد التيتانيوم على خصائص خليط أوكسيد التيتانيوم والقصدير وقد بينت نتائج الاشعة السينية أن موقع القسم انحرف باتجاه قيم الزوايا الأعلى بزيادة نسبة أوكسيد التيتانيوم. أما مورفولوجيا السطح للمادة المتترسبة فقد تم دراستها بواسطة المجهر الماسح الإلكتروني. وقد بينت النتائج أن الحجم الحبيبي للجسيمات النانوية كان يزيد بنسبة أوكسيد القصدير من الحجم الحبيبي (53.6 نانومتر) إلى الحجم الحبيبي (25.5 نانومتر). وكذلك قد تم ملاحظة التغيرات الحاسلة لطيف النفاذية وكذلك فوهة الطاقة البصرية بواسطة قياسات مطيافية النفاذية للأشعة المرئية وفوق البنفسجية.
INTRODUCTION

Mixed oxide systems have attracted considerable attention. The good stability of sensing properties of SnO$_2$ for reducing gases, combined with the good chemical stability of TiO$_2$ at high temperatures, stimulate the study on the applications of TiO$_2$–SnO$_2$. In particular, TiO$_2$–SnO$_2$ system combines the positive features of both materials being used in gas detection [1] and suggested to be applied as high-temperature resistors [2].

It was concluded by K. Zakrzewska and co-workers that high operating temperatures of TiO$_2$ sensors could be reduced to about 770 K as a result of Sn incorporation [3].

There are many different techniques used for depositing tin oxide films: r.f. sputtering, d.c.-magnetron sputtering, thermal evaporation, ion beam deposition, rheotaxial growth and thermal oxidation (RGTO), chemical vapour deposition, spray pyrolysis, successive ionic layer deposition (SILD) and other chemical methods. Sberveglieri has presented a review of the techniques applied for oxide films deposition [4], [5]. All methods discussed require high substrate temperature or post deposition annealing in order to fabricate good quality polycrystalline films. High temperature, however, damages the surface of the films and increases the interface thickness, which has negative effect on the optical properties, especially on the wave guiding. Pulsed laser deposition technique was successfully applied for growing of quality thin films [6].

This technique is also suitable for depositing oxide films at a relative high deposition rate and low cost [7, 8]. In this work, we report on the growth of (TiO$_2$–SnO$_2$) deposits by PLD using 10 ns pulses at 532 nm on Si(111) and glass substrates. The deposits were characterized by X-ray diffraction (XRD) to examine their crystallinity, scanning electron microscope (SEM) to observe the surface structure and UV-visible spectroscopy to investigate the optical properties of the films.

EXPERIMENTAL PROCEDURE

Film preparation

The deposition was carried out using a Q-switched Nd:YAG laser with a second harmonic generation (SHG) at wavelength is 532 nm with pulse width 7 ns and repetition rate 10 Hz. The studied films were prepared by mixed oxides (TiO$_2$–SnO$_2$) films with different SnO$_2$ contents (25%, 50%, and 75%) targets films were grown by pulsed laser deposition on Si(111) and glass substrates kept an on-axis distance of 4 cm from the target. The chamber was kept at vacuum pressure of $10^{-5}$ mbar as shown in Figure (1). The (TiO$_2$–SnO$_2$) disc was ablated from 10-100 pulses (10-20 min) to get single layered thin films. Consequently, the films were deposited by PLD at 400 °C substrate temperature in an O$_2$ pressure $5 \times 10^{-1}$ mbar and laser fluance (1.4) J/cm$^2$. 
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Figure (1) Experimental setup

Film characterization

The crystalline structure of the films was determined by X-Ray Diffraction (XRD) measurements (Philips PW 1050, $\lambda = 1.54 \text{ Å}$) using Cu k$\alpha$. Transmission measurements were performed for a range 300-800 nm using UV-VIS-UV-8800 (Perkin Elmer Company) spectrophotometer. The characterizations included determination of the absorption as a function of incident photon energy, determination of the transmission as a function of incident photon energy and determination the value energy gap. The surface morphology was examined by Scanning Electron Microscopy (SEM–JEOL 7000).

RESULT AND DISCUSSION

Figure (2) shows the XRD patterns of the (TiO$_2$-SnO$_2$) films grown on Si (111) at $T_s = 400 \, ^\circ\text{C}$ at laser flounce 1.4 J/cm$^2$ diffraction peaks located at $2\theta = 28^\circ$ corresponding to Silicon substrates are shown in the Figure below. At SnO$_2$ 25% concentration, showed diffraction peaks located at $2\theta = 26.9^\circ$, $2\theta = 34^\circ$ and $2\theta = 52.1^\circ$ corresponding to the (110), (101) and (211), peaks respectively. At SnO$_2$ content to 50%, diffraction peaks were located at $2\theta = 27.0^\circ$, $2\theta = 34.3^\circ$ and $2\theta = 52.6^\circ$, corresponding to the (110), (101) and (211) peaks respectively. At 75% concentration, showed diffraction peaks located at $2\theta = 27.2^\circ$, $2\theta = 34.5^\circ$ and $2\theta = 53^\circ$ corresponding to the (110), (101) and (211) where the peaks position of the plane was shifted towards higher angle ($2\theta$) values with increasing amounts of SnO$_2$ content. It has been reported that TiO$_2$ crystallizes as anatase but even a small addition of Sn changes the crystallographic structure to that of tetragonal rutile. X-ray diffraction peaks are shifted from the positions characteristic to TiO$_2$-rutile due to the change in the lattice parameters upon the substitution of Sn for Ti. With the increasing tin content, X-ray diffraction lines shift systematically towards positions.
typical for tetragonal, cassiterite form of SnO$_2$. All XRD patterns of films reflect that the crystal lattice of mixed oxide (SnO$_2$-TiO$_2$) did not undergo significant changes. XRD analysis also did not detect the TiO$_2$ phase, these due to the small molecular weight of TiO$_2$ as compared with that of SnO$_2$ and dispersion of this small-grain phase.

![XRD patterns of (TiO$_2$-SnO$_2$) films grown on Si at various SnO$_2$ content.](image)

Figure (2) XRD patterns of (TiO$_2$-SnO$_2$) films grown on Si at various SnO$_2$ content.
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Table (1) the obtained result of the XRD for (TiO$_2$-SnO$_2$)/Si at T=400 °C.

<table>
<thead>
<tr>
<th>sample</th>
<th>2θ (degree)</th>
<th>(hkl)</th>
<th>FWHM$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(75% TiO$_2$-25% SnO$_2$)</td>
<td>26.9</td>
<td>R(110)</td>
<td>0.163</td>
</tr>
<tr>
<td></td>
<td>34</td>
<td>R(101)</td>
<td>0.164</td>
</tr>
<tr>
<td></td>
<td>52.1</td>
<td>R(211)</td>
<td>0.143</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>Si(111)</td>
<td>0.305</td>
</tr>
<tr>
<td>(50% TiO$_2$-50% SnO$_2$)</td>
<td>27</td>
<td>R(110)</td>
<td>0.245</td>
</tr>
<tr>
<td></td>
<td>34.3</td>
<td>R(101)</td>
<td>0.275</td>
</tr>
<tr>
<td></td>
<td>52.6</td>
<td>R(211)</td>
<td>0.191</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>Si(111)</td>
<td>0.305</td>
</tr>
<tr>
<td>(25% TiO$_2$-75% SnO$_2$)</td>
<td>27.25</td>
<td>R(110)</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>34.5</td>
<td>R(101)</td>
<td>0.144</td>
</tr>
<tr>
<td></td>
<td>53</td>
<td>R(211)</td>
<td>0.157</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>Si(111)</td>
<td>0.305</td>
</tr>
</tbody>
</table>

SEM images of the TiO$_2$ mixed with different content of SnO$_2$ (25%, 50%, 75%) are presented in Figure (3) for film deposited at fixed substrate temperature of 400 °C at Oxygen pressure of (5 ×10$^{-1}$ mbar) and 1.4 J/cm$^2$ laser fluence. The grain size decreases with increasing SnO$_2$ content. SEM images show clearly that size and shape of grains are strongly affected by the chemical composition of SnO$_2$-TiO$_2$. Grain growth has been observed for TiO$_2$. Were Addition of SnO$_2$ reduces the grain size.

Table (2) The obtained result of the SEM for (TiO$_2$-SnO$_2$)/Si at T=400 °C.

<table>
<thead>
<tr>
<th>sample</th>
<th>SEM of plane grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(75% TiO$_2$-25% SnO$_2$)</td>
<td>53.6</td>
</tr>
<tr>
<td>(50% TiO$_2$-50% SnO$_2$)</td>
<td>46.2</td>
</tr>
<tr>
<td>(25% TiO$_2$-75% SnO$_2$)</td>
<td>25.5</td>
</tr>
</tbody>
</table>

SEM images of the TiO$_2$ mixed with different content of SnO$_2$ (25%, 50%, 75%) are presented in Figure (3) for film deposited at fixed substrate temperature of 400 °C at Oxygen pressure of (5 ×10$^{-1}$ mbar) and 1.4 J/cm$^2$ laser fluence. The grain size decreases with increasing SnO$_2$ content. SEM images show clearly that size and shape of grains are strongly affected by the chemical composition of SnO$_2$-TiO$_2$. Grain growth has been observed for TiO$_2$. Were Addition of SnO$_2$ reduces the grain size.
Figure (3) SEM images of (TiO$_2$-SnO$_2$) films grown on Si at different SnO$_2$ content %a) 25% b) 50% c) 75.

Figure (4) shows the optical transmittance of the (TiO$_2$-SnO$_2$) films deposited on glass substrate at oxygen pressures ($5 \times 10^{-1}$) mbar and at fixed substrate temperature of 400°C with 1.4 J/cm$^2$ laser fluence energy density. With average thickness (200) nm. It is found that the optical transmission of the (TiO$_2$-SnO$_2$) films increases as SnO$_2$ content is increased. This may be attributed to the fact that new defects are introduced after Sn atoms substitute Ti atoms and enter into TiO$_2$ lattice due to the electronegativity and ionic radius difference between Ti and Sn.

Figure (4) UV-VIS transmittance spectra of the (TiO$_2$-SnO$_2$) films at different SnO$_2$ content at 400°C substrate temperature with laser fluence 1.4J/cm$^2$. 
The optical energy gap (Eg) values of the (TiO$_2$-SnO$_2$) films deposited on glass substrate at constant substrate temperature 400 °C, 1.4J/cm$^2$ laser fluence, and oxygen pressure 5×10$^{-1}$ mbar are determined and found to be increase from 2.9 to 4.1eV with SnO$_2$-content increased as shown in Figure (5). In other words, the optical energy band gap (TiO$_2$-SnO$_2$) thin films become wider as SnO$_2$ content increases and The reason for observed blue shift in the band gap could be attributed to the higher band gap energy of SnO$_2$ ($\approx$ 4.3eV).

**CONCLUSIONS**

The (TiO$_2$-SnO$_2$) mixed oxide thin films have been prepared by PLD with different ratio with the ultimate aim to gain a deeper understanding of the properties of the system.

When the SnO$_2$ concentration further increased, the XRD analysis did not detect the TiO$_2$ phase, these due to the small molecular weight of TiO$_2$. SEM images show clearly that size and shape of grains are strongly affected by the chemical composition of (TiO$_2$-SnO$_2$) Were Addition of SnO$_2$ reduces the grain size to 25.5nm. The band gap energy of (TiO$_2$-SnO$_2$) films increases as SnO$_2$ concentration is increased because the higher band gap energy of SnO$_2$ ($\approx$ 4.3eV).
REFERENCES


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