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THIN SOLID FILMS OF OXIDES, TiO_2, Fe_2O_3, AND SnO_2, PREPARED BY ORGANOMETALLIC

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Résumé - Des films minces de TiO_2, Fe_2O_3, SnO_2 ont été préparés par CVD à partir d'organométalliques. La structure et les caractéristiques de ces films ont été déterminées par diffraction X, microscopie électronique, diffraction électronique et absorption UV. Le comportement photoélectrochimique de ces dépôts sur monocristal de silicium est également mentionné.

Abstract - Thin oxide films of TiO_2, Fe_2O_3, and SnO_2, have been prepared by the organometallic chemical vapor deposition (MO-CVD) technique. The structure and character of these oxide films were determined by X-ray diffraction, electron microscopy, electron diffraction and UV absorption. These properties are reported. The photoelectrochemical behavior of these films on silicon single crystals as electrodes are also reported.

1- INTRODUCTION

TiO_2, Fe_2O_3 and SnO_2 in pure form are wide-bandgap semiconductors- [1]. These films have high transparency in the visible spectral region. These oxide films have found applications in electronics, optoelectronics, solar cells and display devices [2,3]. A variety of techniques, including reactive sputtering, reactive evaporation, ion-beam evaporation and chemical vapor deposition and hydrolysis of the respective halides or alkoxides are employed for the growth of TiO_2, Fe_2O_3, and SnO_2 thin films [4]. In recent years, organometallic-CVD has emerged as a successful way for the growth of these thin films. The MO-CVD techniques were used over the past several years and they have often yielded superior quality films than those grown by the conventional CVD or physical methods [1].

2- EXPERIMENTS

The equipment for obtaining films by the MO-CVD method is quite simple, the diagram of experimental equipment is showed in fig.1.

![Diagram of experimental equipment](image-url)

Fig. 1 Experimental equipment : A. reactor B. furnace C. substrates D. source E. doped source F. valve G. flow meter H. exhaust
Thin films of TiO$_2$, Fe$_2$O$_3$, and SnO$_2$ were grown by pyrolysis and oxidation of (C$_4$H$_8$O)$_4$TiFe(C$_3$H$_5$)$_2$ and (CH$_3$)$_4$Sn; with O$_2$-N$_2$ mixtures as carrier gas; deposition was carried out on hot glass or silicon substrates at 300°C-480°C. The method is based on the following reactions:

\[
\text{Source} \quad \begin{cases} 
(C_4H_8O)_4Ti & \text{O}_2 + N_2 \\
Fe(C_3H_5)_2 & \rightarrow TiO_2 \\
(CH_3)_4Sn & \Rightarrow Fe_2O_3 \\
& \text{SnO}_2
\end{cases} \\
\text{300-480°C} \quad + \quad \text{gaseous organic products}
\]

The optimal deposition conditions are listed in Table 1.

**Table 1:** Optimal deposition conditions for TiO$_2$, Fe$_2$O$_3$ and SnO$_2$ films

<table>
<thead>
<tr>
<th>Compound</th>
<th>growth temp. (°C)</th>
<th>source temp. (°C)</th>
<th>flow rate of N$_2$ or O$_2$ through the source (ml/min)</th>
<th>flow rate of O$_2$ (ml/min)</th>
<th>total gas flow rate (l/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>400-480</td>
<td>120</td>
<td>N$_2$</td>
<td>60</td>
<td>45</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>300-350</td>
<td>120</td>
<td>O$_2$</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>410-470</td>
<td>25</td>
<td>N$_2$</td>
<td>80</td>
<td>80</td>
</tr>
</tbody>
</table>

The P, As and F-doped SnO$_2$ films (thickness-1500Å) were deposited on glass at 430°C in the following conditions (Table 2).

**Table 2:** Deposition conditions for different doped SnO$_2$ films (A* is P, As or F)

<table>
<thead>
<tr>
<th>Doped films</th>
<th>Atomic ratio (A*/Sn)</th>
<th>Flow rate of O$_2$ (ml/min)</th>
<th>Growth rate (Å/min)</th>
<th>Sheet resistance (ohm/cm$^2$)</th>
<th>Transmission T (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$.P</td>
<td>0.01</td>
<td>48</td>
<td>500</td>
<td>32</td>
<td>95</td>
</tr>
<tr>
<td>SnO$_2$.As</td>
<td>0.01</td>
<td>55</td>
<td>270</td>
<td>38</td>
<td>86</td>
</tr>
<tr>
<td>SnO$_2$.F</td>
<td>0.02</td>
<td>0</td>
<td>800</td>
<td>34</td>
<td>82</td>
</tr>
</tbody>
</table>

The growth rates of these films are shown in Fig. 2.
The films were characterized by (D/MAX*rA) X-ray diffraction, classical scanning electron microscopy, transmission electron microscopy and by UV spectrometry. The results are presented on the figures 3-4-5.

Fig. 2: Growth rates vs substrate temperature (a): TiO₂; (b): Fe₂O₃; (c): SnO₂

The films were characterized by (D/MAX*rA) X-ray diffraction, classical scanning electron microscopy, transmission electron microscopy and by UV spectrometry. The results are presented on the figures 3-4-5.

Fig. 3: X-ray diffraction patterns A: TiO₂ (rutile); B: TiO₂ (anatase); C: α-Fe₂O₃; D: amorphous Fe₂O₃; E: SnO₂
Fig. 4 (a) Diffraction ring of polycrystalline TiO$_2$ deposited on (111) single crystal silicon at 480°C

Fig. 4 (b) Electron diffraction ring of amorphous Fe$_2$O$_3$ deposited on glass at 450°C

Fig. 4 (c) Morphology of SnO$_2$ film deposited on (111) single crystal silicon at 430°C

Fig. 4 (d) Morphology of P-doped (P/Si atomic ratio 0.26) SnO$_2$ film deposited on a (111) single crystal silicon at 430°C

Fig. 5 UV absorption spectrum of 1500Å thick films deposited on glass
a: a-Fe$_2$O$_3$; b: TiO$_2$; c: SnO$_2$. 
Fig. 6 Variation of the photocurrent ($I$) in function of the potential ($V$ vs HgO) of different films deposited on single crystal silicon as photocathode.

A: C (solution) : 1 mol KOH

- $I$ (photocurrent) : 53 mW cm$^{-2}$
- $v$ (sweep rate) : 100 mV sec$^{-1}$

B: C : 1 mol KOH

- $I$ : 110 mW cm$^{-2}$
- $v$ : 100 mV sec$^{-1}$

(a) $P+/P$-Si
- b, b' $P+/P$-Si/Fe$_2$O$_3$
- a, a' $P$/P-Si
- a, b irradiated
- a', b unirradiated

C: C : 0.2 mol Na$_2$SO$_4$

- $I$ : 800 mW cm$^{-2}$
- $v$ : 50 mV sec$^{-1}$

1 unirradiated
2 P-Si irradiated
3 P-Si/SnO$_2$ irradiated
3- CONCLUSIONS

In this paper the optimal deposition conditions for TiO₂, Fe₂O₃ and SnO₂ films carried out by MOCVD technique are reported. The behavior of growth rates of these films in function of substrate temperatures are similar (fig.2). The highest growth rates of TiO₂, Fe₂O₃ and SnO₂ films are 11.5 A/min (700°C), 380 A/min (400°C), 900 A/min (410°C) respectively.

Polycrystalline TiO₂ exhibits either a rutile or anatase structure. The results of the X-ray diffraction indicate that TiO₂ crystallizes with the rutile structure when the deposition occurs above 400°C and the anatase structure when the film grows below 400°C on single crystal (111) Si substrates. The polycrystalline films of Fe₂O₃ are α-Fe₂O₃ when deposited at 300°C-350°C on single crystal (111) Si substrates; when deposition is made at 450°C on glass substrates amorphous Fe₂O₃ is obtained. The films of SnO₂ are generally polycrystalline and their X-ray diffraction patterns show a preferred orientation connected with the strongest (110) line. These polycrystalline films (thickness : 1500 Å) have a high transparency (85-95%) in the visible spectral region and show high electrical resistivities at room temperature (ρ > 10 Ω cm). Doped films (1000-3000 Å thick) with square resistance values of 30-40 ohm/cm² and light transmission up to 80-95%, in the visible spectral region can be readily prepared. The films with the P(As or F) /Sn atomic ratio approaching 0.01-0.02 show similar growth behaviour and yield maximum conductivity.

The P-doped (P/Si atomic ratio 0.01) yields films of higher conductivity (32 ohm/cm²) without loss of optical transmission (95%). When the P/Sn atomic ratio is 0.25, the films exhibited rapid transition from the polycrystalline to the amorphous state (fig.4(d)). The photoelectrochemical properties of these films on (111) single crystals silicon as electrodes were shown; the photoresponse of these films on silicon photocathode increase the potential of hydrogen evolution and shifts it to the positive direction (fig.6).

REFERENCES


