REALIZATION OF SOLAR CELLS BASED ON SILICON/OXIDE JUNCTIONS

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Transparent and conductive films of SrTiO$_3$, ITO, and Tl$_2$O$_3$ have been deposited by R.F. cathodic sputtering and by anodic oxidation onto Si substrates in order to realize SIS cells. A photoconversion efficiency of 8.8% has been obtained for Si/SiO$_x$/Tl$_2$O$_3$ cells. On the other hand for Si/SiO$_x$/SrTiO$_3$(ITO) the photoconversion efficiency is lower than 1% because of the too large thickness of the SiO$_x$ interfacial layer.

Transparent and conductive films of SrTiO$_3$, Indium Tin Oxide (ITO), and Tl$_2$O$_3$ have been deposited by R.F. cathodic sputtering and by anodic oxidation (tables I and II).

SrTiO$_3$ deposited at room temperature is amorphous and is relatively transparent to visible light (E$_g$ = 3.0 eV, $\alpha$ = 10$^4$ cm$^{-1}$). The Fermi level in this film is pinned at about 0.6 eV under the conduction band edge (E$_F$ = 4.0 eV) by the energy states Ti$^{3+}$:3d$^1$ (t$_{2g}$) originating from Ti-O dangling bonds. These energy levels are also responsible for the electronic transport in this film ($\mu$e(25°C) = 10$^{-1}$ cm$^2$/V·s, E$_a$ = 0.07 eV).

SrTiO$_3$ deposited at 250°C under a controlled reductive atmosphere (60% Ar + 40% H$_2$) is partially crystallized (noted as SrTiO$_3$ (p.c.)) and its composition is, in fact, SrTiO$_{2.8}$. The band gap of the film is reduced to 2.5 eV by the interaction between the Ti$^{3+}$:3d$^1$ (t$_{2g}$) non-bonding states. The Fermi level is just near the bottom of the conduction band. The electronic transport is assured by the free electrons in the conduction band ($\mu$e(25°C) = 60 cm/V·s, E$_a$ = 0.03 eV)$^2$.

The energy band diagrams of the films are reported on the Fig. 1.

ITO is amorphous when deposited at room temperature and becomes crystallized when deposited at 250°C. Tl$_2$O$_3$ crystallizes in the same structure as ITO.

Both ITO and Tl$_2$O$_3$ are degenerated n$^+$-type semiconductors. Tl$_2$O$_3$ is transparent to visible light (like ITO) in spite of its small band energy gap value (E$_g$ = 1.4 eV). The conduction band edge of Tl$_2$O$_3$ (E.A. = 5.0 eV) is 0.8 eV lower than that of ITO (E.A. = 4.2 eV). All these phenomena can be explained on the basis of the band energy diagram common for ITO and Tl$_2$O$_3$ (Fig. 2). The proposed energy diagram model is in good agreement with that proposed by Switzer$^3$.

Because of their transparency, electrical conductivity, and electron affinity, thin films of SrTiO$_3$ (p.c) and ITO have been deposited onto p-Si (100) face, and that of Tl$_2$O$_3$, onto n-Si (100) face, to realize the SIS (Semiconductor-Insulator-Semiconductor) tunnel solar cells (Fig. 3).
FIGURE 1  Energy band diagram of SrTiO$_3$ films, amorphous (a) and partially crystallized (b).
### TABLE I
R.F. sputtering deposition condition.

<table>
<thead>
<tr>
<th>Film</th>
<th>Atmosphere Compos.</th>
<th>Pressure</th>
<th>Sputtering power</th>
<th>Target-Sub. distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO₃</td>
<td>Ar 60% H₂ 40%</td>
<td>1.5 Pa</td>
<td>150 W</td>
<td>5 cm</td>
</tr>
<tr>
<td>ITO</td>
<td>Ar 100%</td>
<td>0.5 Pa</td>
<td>55 W</td>
<td>7 cm</td>
</tr>
</tbody>
</table>

### TABLE II
Anodic oxidation condition for Ti₂O₃.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Solution</th>
<th>Current intensity</th>
<th>Electrode potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>CH₃COOTi 0.5 M</td>
<td>5 mA/cm²</td>
<td>* 0.5 V/SCE</td>
</tr>
<tr>
<td>Si</td>
<td>+ NaOH 1 M</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Under the illumination of 150 W Xe-Lamp.

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**FIGURE 2** Energy band diagram of ITO (a) and Ti₂O₃ (b) films.

**FIGURE 3** Energy band diagram of SIS solar cells.
The Schottky-barrier heights ($\phi_s$) of the solar cells.

<table>
<thead>
<tr>
<th>Cell</th>
<th>$\phi_s$ measured by transient photocurrent</th>
<th>$\phi_s$ calculated from the difference of $E_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-p/SiOx/ITO</td>
<td>0.90 eV</td>
<td>0.93 eV</td>
</tr>
<tr>
<td>Si-p/SiOx/SrTiO$_3$</td>
<td>1.10 eV</td>
<td>1.23 eV</td>
</tr>
<tr>
<td>Si-n/SiOx/Ti$_2$O$_3$</td>
<td>1.00 eV</td>
<td>1.00 eV</td>
</tr>
</tbody>
</table>

The ohmic back contact is assured by silver paste on p-Si, and by an In-Ga eutectic alloy on n-Si. Silver forms the ohmic contact on p-Si because of the alloying effects between Ag and SiO$_x$.

Different etching processes of silicon surfaces have been used in order to minimize the influence of the interface states. Thus there is no Fermi level pinning effects observed (Table III).

The efficiency of the Si-p/SiOx/SrTiO$_3$ (500Å) and the Si-p/SiOx/ITO (100Å) cells are small ($\eta < 1\%$) because of the existence of a too thick insulating interfacial layer of SiO$_x$ ($d > 20\AA$) which is inherent to the experimental conditions (Fig. 4 and 5).

In the case of the Si-n/SiOx/Ti$_2$O$_3$ (1000Å) cells, the thickness of the SiO$_x$ layer is appropriate ($10\AA < d < 20\AA$); an efficiency of 8.8% has thus been obtained (Fig. 6). A semi-theoretical study demonstrates that an efficiency of 12.3%, close to that obtained by A. Switzer$^3$, can be achieved by optimizing the etching process of the silicon surface$^2$.

![FIGURE 4 I-V characteristics of the solar cells: (d$_{SiOx} > 20\AA$) (1) Si-p/SiOx/ITO (2) Si-p/SiOx/SrTiO$_3$.](image-url)
A back-wall MIS solar cell (Ag/SiOx/Si-n/ITO) using ITO as transparent ohmic contact material has been demonstrated to be interesting if one can reduce the silicon thickness.

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REFERENCES
