REALIZATION OF SOLAR CELLS BASED ON SILICON/OXIDE JUNCTIONS

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Transparent and conductive films of SrTiO₃, ITO, and Ti₂O₃ 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/Ti₂O₃ cells. On the other hand for Si/SiO_x/SrTiO₃(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 SrTiO₃, Indium Tin Oxide (ITO), and Ti₂O₃ have been deposited by R.F. cathodic sputtering and by anodic oxidation (tables I and II).

SrTiO₃ deposited at room temperature is amorphous and is relatively transparent to visible light ($E_g = 3.0$ eV, $\alpha = 10^4 \cdot \text{cm}^{-1}$). 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 $\text{Ti}^{3+}:3d^1$ (t_{2g}) originating from Ti-O dangling bonds¹. These energy levels are also responsible for the electronic transport in this film ($\mu_e(25^\circ\text{C}) = 10^{-1} \cdot \text{cm}^2/\text{V}\cdot\text{s}$, $E_a = 0.07$ eV).

SrTiO₃ deposited at 250°C under a controlled reductive atmosphere (60% Ar + 40% H₂) is partially crystallized (noted as SrTiO₃ (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 $\text{Ti}^{3+}:3d^1$ (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 ($\mu_e(25^\circ\text{C}) = 60 \text{ cm}^2/\text{V}\cdot\text{s}$, $E_a = 0.03$ 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. Ti₂O₃ crystallizes in the same structure as ITO.

Both ITO and Ti₂O₃ are degenerated n⁺-type semiconductors. Ti₂O₃ 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 Ti₂O₃ (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 Ti₂O₃² (Fig. 2). The proposed energy diagram model is in good agreement with that proposed by Switzer³.

Because of their transparency, electrical conductivity, and electron affinity, thin films of SrTiO₃ (p.c) and ITO have been deposited onto p-Si (100) face, and that of Ti₂O₃, onto n-Si (100) face, to realize the SIS (Semiconductor-Insulator-Semiconductor) tunnel solar cells (Fig. 3).

FIGURE 1 Energy band diagram of SrTiO₃ films, amorphous (a) and partially crystallized (b).

TABLE I
 R.F. sputtering deposition condition.

Film	Atmosphere		Sputtering power	Target-Sub. distance
	Compos.	Pressure		
SrTiO ₃	Ar 60% H ₂ 40%	1.5 Pa 0.5 Pa	150 W	5 cm
ITO	Ar 100%	0.5 Pa	55 W	7 cm

 TABLE II
 Anodic oxidation condition for Ti₂O₃.

Substrate	Solution	Current intensity	Electrode potential
Ti Si	CH ₃ COOTl 0.5 M + NaOH 1 M	5 mA/cm ²	* 0.5 V/SCE

* Under the illumination of 150 W Xe-Lamp.

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

FIGURE 3 Energy band diagram of SIS solar cells.

TABLE III
The Schottky-barrier heights (ϕ_B) of the solar cells.

Cell	ϕ_B measured by transient photocurrent	ϕ_B calculated from the difference of E_F
Si-p/SiOx/ITO	0.90 eV	0.93 eV
Si-p/SiOx/SrTiO ₃	1.10 eV	1.23 eV
Si-n/SiOx/Tl ₂ O ₃	1.00 eV	1.00 eV

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 SiOx⁴.

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/SrTiO₃ (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 SiOx ($d > 20\text{\AA}$) which is inherent to the experimental conditions (Fig. 4 and 5).

In the case of the Si-n/SiOx/Tl₂O₃ (1000Å) cells, the thickness of the SiOx layer is appropriate ($10\text{\AA} < d < 20\text{\AA}$); 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. Switzer³, can be achieved by optimizing the etching process of the silicon surface².

FIGURE 4 I-V characteristics of the solar cells: ($d_{\text{SiOx}} > 20\text{\AA}$) (1) Si-p/SiOx/ITO (2) Si-p/SiOx/SrTiO₃.

FIGURE 5 I-V characteristics of the Si-p/SiO_x/ITO cells: (1) Experimental curve (2) Expected curve if $d_{\text{SiO}_x} < 20 \text{ \AA}$.

FIGURE 6 I-V characteristics of the Si-n/SiO_x/Ti₂O₃ cell ($10 \text{ \AA} < d_{\text{SiO}_x} < 20 \text{ \AA}$).

A back-wall MIS solar cell (Ag/SiO_x/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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