

PROTECTION OF PHOTOANODES AGAINST PHOTO-CORROSION BY SURFACE DEPOSITION OF OXIDE FILMS: CRITERIA FOR CHOOSING THE PROTECTIVE COATING.

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Two strategies to solve the problem of instability of photoanodes against photocorrosion have been explored. The photocorrosion of photoanodes generally occurs when they enter the fabrication of efficient photoelectrochemical cells (i.e. showing high values of the open circuit voltage and photocurrent density).

One of these strategies consists of protecting the photoanode against photocorrosion by a non-conducting oxide film deposited on its surface. The oxide must have a cationic valence band, or valence energy states, falling either above, or at the same level as, the top of the valence band of the anode. The significant photocurrent observed with the n-GaAs/Sr_{0.98}Na_{0.01}Ce_{0.01}TiO₃ hybridelectrode structure confirms the validity of the model.

The second possibility deals with the protection of the photoanode by a conducting oxide film in which the carrier transport occurs, close to the Fermi level, via either a partially filled band or a sufficiently high density of localized states. We have illustrated this method of protection by depositing n-SrTiO₃ on n-GaAs. The n-SrTiO₃ films have the Fermi level pinned within the forbidden band by Ti:3d(t_{2g}) energy states. The corresponding electrochemical cells exhibit photoconversion efficiency as high as 18% for an illumination of 5 mW/cm².

INTRODUCTION

Photoelectrochemistry, i.e. the conversion of solar energy with a semiconductor-electrolyte junction, has several advantages over photovoltaic conversion:

- elimination of expensive manufacturing steps like differential doping, grid deposition.
- simplicity of the junction, which is just a semiconductor immersed in an electrolyte.
- the photopotential, and hence the e.m.f. of the cell, can be varied as it depends upon the choice of the redox couple.

Many papers and recent patents have thus shown that photo-electrochemical cells can have high conversion yields, particularly the cells using n-semiconducting photoanodes with high carrier mobility and narrow forbidden band energy gap (n-GaAs, nSi, n-CdSe_{0.65}Te_{0.35} ...)¹.

There is, however, an obstacle to the production of high-yield cells with high open circuit voltage (electromotive force): n-type semiconducting photoanodes (with high carrier mobility and a narrow forbidden band) are generally chemically unstable when they are illuminated in an aqueous medium.

Various strategies to solve this instability problem have been explored. The most attractive is protection of the semiconductor by a thin film, resistant to the electrolyte and transparent to sunlight.

In this prospect Horowitz and Garnier indeed obtained a very stable (≈ 100 h) photoanode in aqueous $\text{Fe}(\text{CN})_6^{4-/3-}$, by surface coating n-GaAs with a 400 Å film of conducting poly(3-methylthiophene). Moreover, the conversion yield was as high as 10%². Note however, that one does not know if the “efficient” junction occurs at the GaAs/polythiophen interface (the electrolyte would then behave as a “transparent contact”) or if the electrolyte plays a determining role in the formation of an efficient Schottky-type junction with the photoanode².

On the other hand, poor results (noticeable drop in the conversion yield, rapid “lifting” of the protective coating) were obtained with semiconductor oxide protectants (Table I)^{3,4,5}.

This difference could be attributed to an infortunate choice of the

TABLE I
Unstable photoanodes protected by a stable semiconducting oxide film.

Protective coat	Coating process	Photoanode (n-type semiconductor)	Conversion yield	Ref.
non conducting (25°C) 10^8 $\Omega.cm$				
non conducting (25°C) 10^{-2} $\Omega.cm$				
TiO ₂	R.F. sputtering	GaAs		3
		Si		
	C V D	GaAs InP		4
	Electrochemical coating	Si	5	
		CdSe		
Al ₂ O ₃	R.F. sputtering	Si	5	
		GaAs	3	
		CdSe	3	
	Electrochemical coating	Si	5	
		CdSe		
Nb ₂ O ₅	Electrochemical coating	GaAs	3	
n-SnO ₂	spray	GaAs	3	
		Si	5	
		CdSe	5	

oxides, listed in Table I, which do not have the appropriate electronic properties.

However that may be, there is to our knowledge no model bringing forward the mechanisms of charge transfer that must occur in the protective film in order to get high conversion yield.

Note, first of all, that broadly speaking an oxide can be amorphous or crystallized, stoichiometric or defect bearing, conducting or non conducting. It should thus be possible to satisfy the criteria set out below for easy carrier transport in the protective film.

CRITERIA FOR CHOOSING PROTECTIVE OXIDE FILMS FOR THE PHOTOANODE

Either insulating or conducting oxides can be envisaged, provided their properties differ from those of the “low-performance” materials listed in Table I.

Protection by an non-conducting oxide: EIS structure (Electrolyte-Insulator-Semiconductor).

We first note that the non-conducting oxides listed in Table I have large band gap:

$$E_g(\text{TiO}_2) = 3.0\text{eV} \quad (5)$$

$$E_g(\text{Al}_2\text{O}_3) = 4.0\text{eV} \quad (6)$$

$$E_g(\text{Nb}_2\text{O}_5) = 2.9\text{eV} \quad (7)$$

Their valence bands are, therefore, below that of the photo-anode they protect, which have small optical gaps ($E_g < 2\text{eV}$). Figure 1 is an energy diagram of the photoanode-film-electrolyte junction. It clearly shows that the tunnel effect is the only way for a photo-produced hole to cross the protective film and oxidize reduced species in the electrolyte.

If the electrolyte may reasonably be thought to behave as a metal (relative to the non-conducting oxide and to the photoanode), it is then clear that useful EIS structures must have an insulating coating of less than 30\AA : we indeed recently showed that in metal-insulator-semiconductor (MIS) structures, the insulator thickness for tunneling-charge-transport to occur should not exceed 20\AA ⁷.

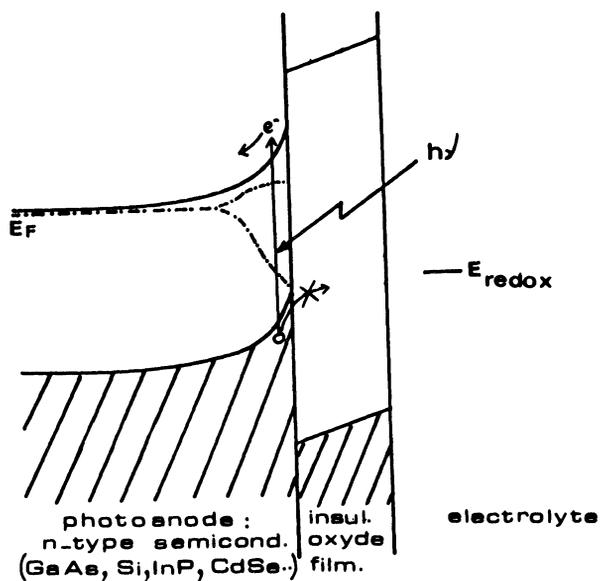


FIGURE 1 An EIS solar cell. Photo-generated holes cannot tunnel through the oxide film if its thickness, e , exceeds 10 Å.

This was not the case for the heterojunctions listed in Table I, since the films were over 40Å thick^{3,4,5}. Hence it was very difficult for photo-holes to tunnel through them (Figure 1). Confinement of the photo-hole at the photoanode/film interface is then unavoidable. This either produces a high recombination rate of the photo-carriers, and hence a drop in the performances, or initiates corrosion of the photoanode leading to lifting of the film^{3,4,5}.

EIS structures should thus have oxide layers of less than 20Å. This is technologically difficult to perform.

Thicker oxide films would be acceptable, however, if carrier confinement could be prevented by making the photo-holes migrate in the valence band of the oxide (Figure 2). It implies that the top of the valence band of the oxide should fall either above or at the same level as the top of the valence band of the photoanode (Figure 2). This seems difficult to fulfill in practice, because we know of no transparent oxide in which the top of the valence band (of anionic character, as it occurs for the oxides listed in Table I) falls high enough.

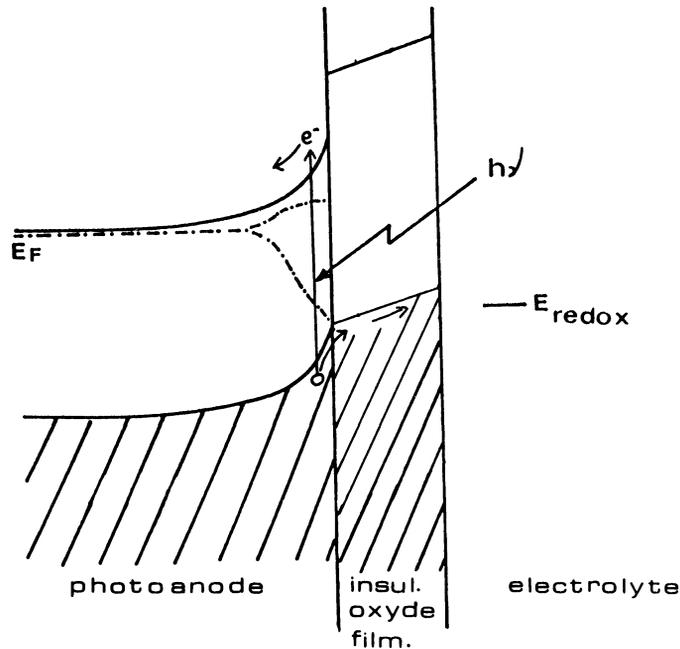


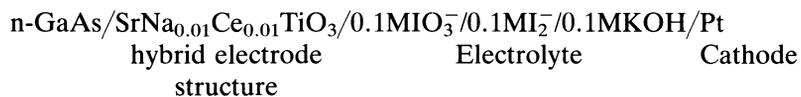
FIGURE 2 An "ideal" EIS solar cell. Photo-generated holes cross the insulator via the valence band.

Note, however, that charge transport through a protective non-conducting film could occur in a valence band, provided we use not the intrinsic anionic valence band of the oxide, but cationic, extrinsic or intrinsic, valence band or valence levels (Figure 3).

This opens the field of investigation, since a wide range of oxides could satisfy this condition.

Table II gives some examples of significant oxides which should efficiently protect n-GaAs photoanodes from photocorrosion: the cationic valence levels quoted in Table II are indeed close to the top of the valence band of GaAs ($E_v = 5.4\text{eV}^{8,9-14}$).

Our recent results using this strategy deal with photoelectrochemical cells with the following structure:



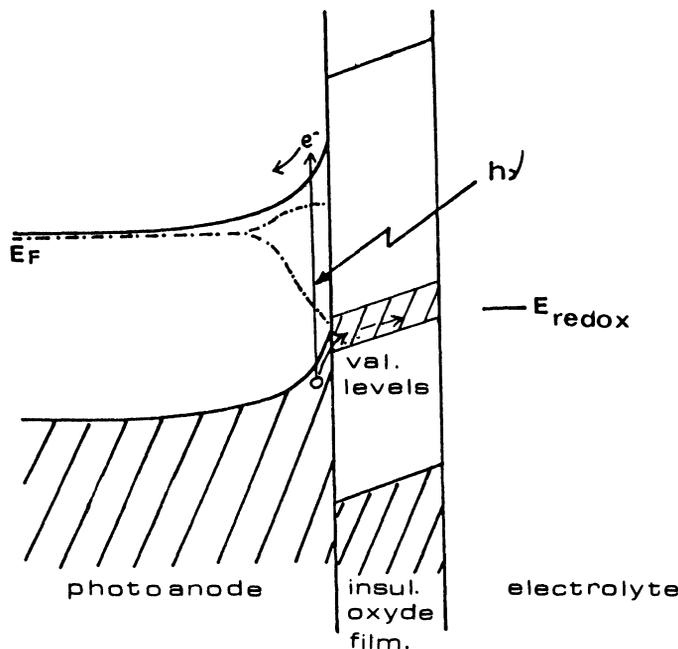


FIGURE 3 A "practical" EIS solar cell. Photogenerated holes cross the insulator via a cationic valence band (C.V.B.).

The $Ce^{3+}:4f^1$ energy states should indeed be located slightly above the valence band edge of GaAs (Table II) and thereby allow the transfer of the photogenerated holes through the film (Figure 3).

For comparison, the n-GaAs/SrTiO₃ heterojunctions sharing undoped SrTiO₃ as a coating, were considered.

An r.f. sputtering deposition technique was used to deposit the Sr_{0.98}Na_{0.01}Ce_{0.01}TiO₃ and SrTiO₃ films, on the (100) face of the n-GaAs substrate, as it generally gives rise to highly compact films adhering tightly to the substrate.

The sputtering targets (of 75 mm diameter) were made either of pelletized insulating Sr_{0.98}Na_{0.01}Ce_{0.01}TiO₃ or SrTiO₃ powders.

To obtain reproducible conditions the following process was used (for both undoped and Ce-doped samples):

- preliminary vacuum: 10⁻⁵ Pa
- atmosphere composition: Ar (100%)

TABLE II
Some likely protective oxides for coating n-GaAs against photocorrosion.

Photoanode	Valence band edge (located vs. the vacuum level) E_V (eV) (ref. 2)	non conducting oxide ($p > 18^8 \Omega \cdot \text{cm}$)	cationic valence levels likely to intervene in the transport process of Figure 3		Corresponding energy level position (eV, vs. vacuum level)	Ref.
			Extrinsic levels	Intrinsic levels		
n-GaAs	5.5	TiO_2 doped with Mn^{2+} or Co^{2+}	$\text{Mn}^{2+}; \text{eg}^2$		5.2	10,
			$\text{Co}^{2+}; \text{t}_{2g}^2$			11
n-GaAs	5.5	SrTiO_3 doped with Ce^{3+}	$\text{Ce}^{3+}; 4f$		5.2	12,
						13
		LaCrO_3		$\text{Cr}^{3+}; 3d^3$	5.4	14
		MnTiO_3		$\text{Mn}^{2+}; \text{eg}^2$	5.4	15

- pressure: 1 Pa
- power supply: 200 W (13, 56 MHz)
- target-to-substrate distance: 4 cm
- film thickness: 0.6 μm (sputtering time: 60').

Details concerning the films analysis and texture, the conductivity and photoconductivity measurements will be reported separately. The non-conducting ($\sigma_{(25^\circ\text{C})} \approx 10^{-10}\Omega^{-1}\text{cm}^{-1}$) deposits were partially crystallized but had the expected stoichiometry. Finally, the photoconductivity spectra of the films gave evidence of subbandgap $\text{Ce}^{3+}:4f^1$ energy levels at about 1.6eV below the conduction band⁷.

Figure 4 shows the photocurrent as a function of the potential difference across the cells which were used as generators. The significant current observed with the n-GaAs/Sr_{0.98}Na_{0.01}Ce_{0.01}TiO₃ heterojunction confirms the validity of the model. It is probable that greater photocurrents could be obtained by increasing the amount of Ce^{3+} .

Figure 4 also shows that the n-GaAs/SrTiO₃ heterojunction gives

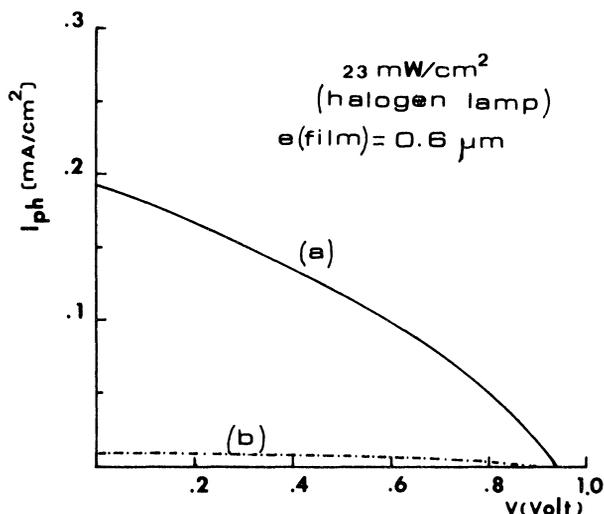


FIGURE 4 Photo-current vs. potential curves for:
 a) n-GaAs/Sr_{0.98}Na_{0.01}Ce_{0.01}TiO₃/0.1MIO₃⁻/0.1MI⁻/0.1MKOH/Pt
 b) n-GaAs/SrTiO₃/0.1MIO₃⁻/0.1MI₃⁻/0.1MKOH/Pt cells

practically no response. This could be expected since SrTiO_3 is not here doped by Ce^{3+} , and it is virtually impossible for photoholes to tunnel through the film (film thickness $\geq 20\text{\AA}$ (Figure 1)).

Protection by a conducting oxide: ESS (Electrolyte-semiconductor-semiconductor) structures.

The disappointing results obtained by previous authors with the heterojunctions $n\text{-GaAs}/n\text{-SnO}_2$, $n\text{-Si}/n\text{-SnO}_2$ and $n\text{-CdSe}/n\text{-SnO}_2$ (Table I) may be interpreted on the basis provided by Figure 5, i.e., the thickness (W) of the space-charge region could be eliminated by protecting the $n\text{-GaAs}$ with a degenerate oxide coat having a consequently metallic conductivity.

ITO (90% In_2O_3 + 10% SnO_2) could be a suitable choice since it is the "perfect" degenerate semiconductor, combining both transparency and metallic conductivity. Unfortunately, we have shown recently that, quite unexpectedly, the metallic conductivity of ITO does not prevent the formation of a space charge region at the ITO/

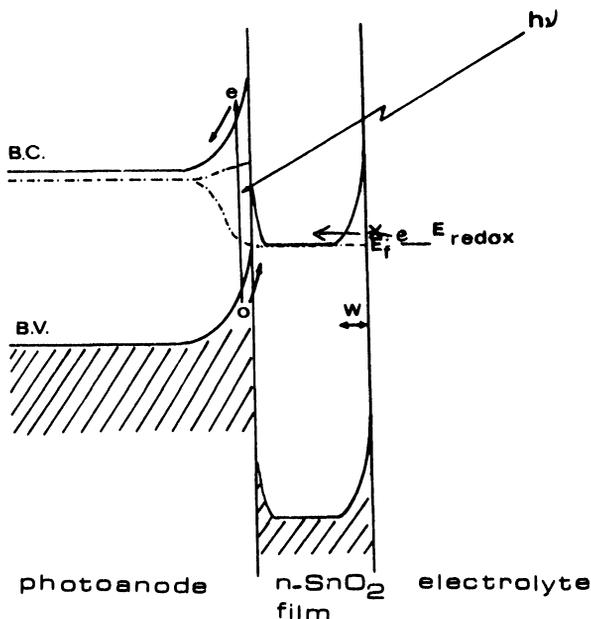


FIGURE 5 $n\text{-GaAs}/n\text{-SnO}_2$ /electrolyte junction.

electrolyte interface⁷. This space-charge region, which is over 30Å thick even for heavily n-type doped films (10^{20} – 10^{21} cm⁻³), is obviously incompatible with efficient carrier tunneling across the ITO/electrolyte interface⁷. In fact, such a space-charge probably occurs for most of transparent degenerate semiconductors (n^+ In₂O₃, n^+ Tl₂O₃...).

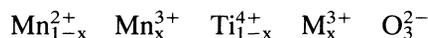
It thus appears that photoanodes cannot be “efficiently” protected, neither by an ITO coating nor by most of others transparent coatings having metallic conductivity.

Despite these comments, successful protection of photoanodes by a conducting oxide is not improbable. In fact, photogenerated holes at the semiconductor surface should, in principle, cross the protective film to react with the electrolyte, provided that the carrier transport occurs close to the Fermi level, E_F , of the film via:

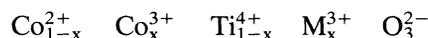
- either a partially filled band,
- or a sufficiently high density of localized states, within which E_F is located.

The oxide should also have a low electron affinity so that an electric field gradient (ΔE) could be set up, to activate the transport of holes towards the electrolyte (Figure 6).

Oxides such as those below could be suitable:



and



where $M^{3+} = \text{Cr}^{3+}$ for example.

The electronic affinity of these titanate oxides which are likely to have the illmenite structure, defined by the energy of the bottom of the $\text{Ti}:3d(t_{2g})$ conduction band, should indeed be small¹⁵. Furthermore, the Fermi level should be trapped in the Mn or Co band, as it is partially filled. It follows that efficient photo-hole transport in the film should use this band according to the process shown in Figure 6.

Note that a deposit of n-SrTiO₃ could also be suitable because:

- the electron affinity of SrTiO₃ is low (3.4eV^{12}).

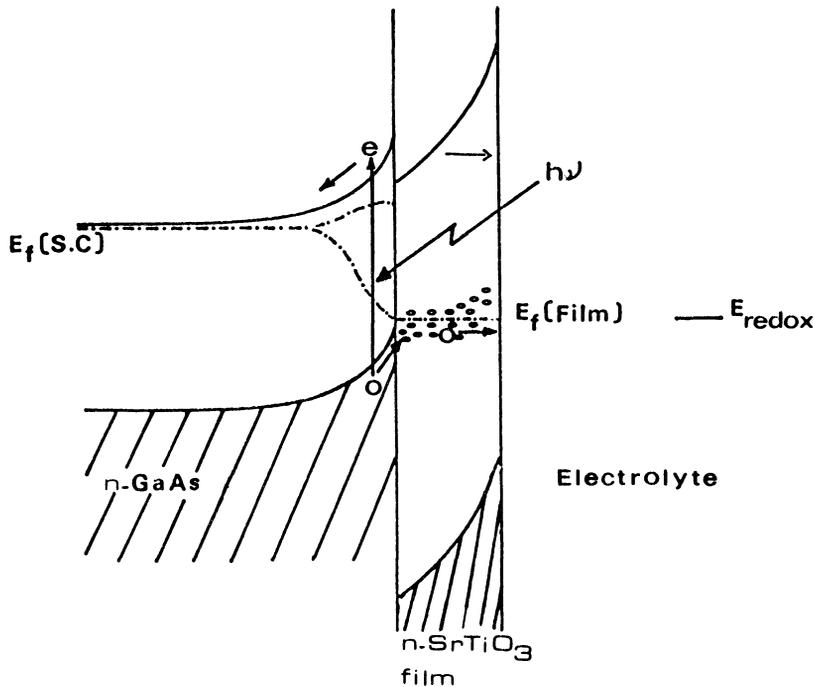


FIGURE 6 Charge transport mechanism in the conducting protective film.

— when it is prepared under suitable conditions (a 40% H_2 + 60% Ar mixture can be used as a sputtering atmosphere; the other deposition parameters are identical to those mentioned above for undoped and Ce-doped $SrTiO_3$), the Fermi level can be trapped within the forbidden band by $Ti:3d(t_{2g})$ energy states¹⁵.

We have thus demonstrated the second strategy of protection by depositing $n-SrTiO_3$ on $n-GaAs$. As expected, we obtained promising results with the following cell:

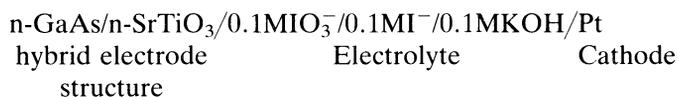


Figure 7 indeed shows conversion yields as high as 18% for an illumination of 5 mW/cm^2 .

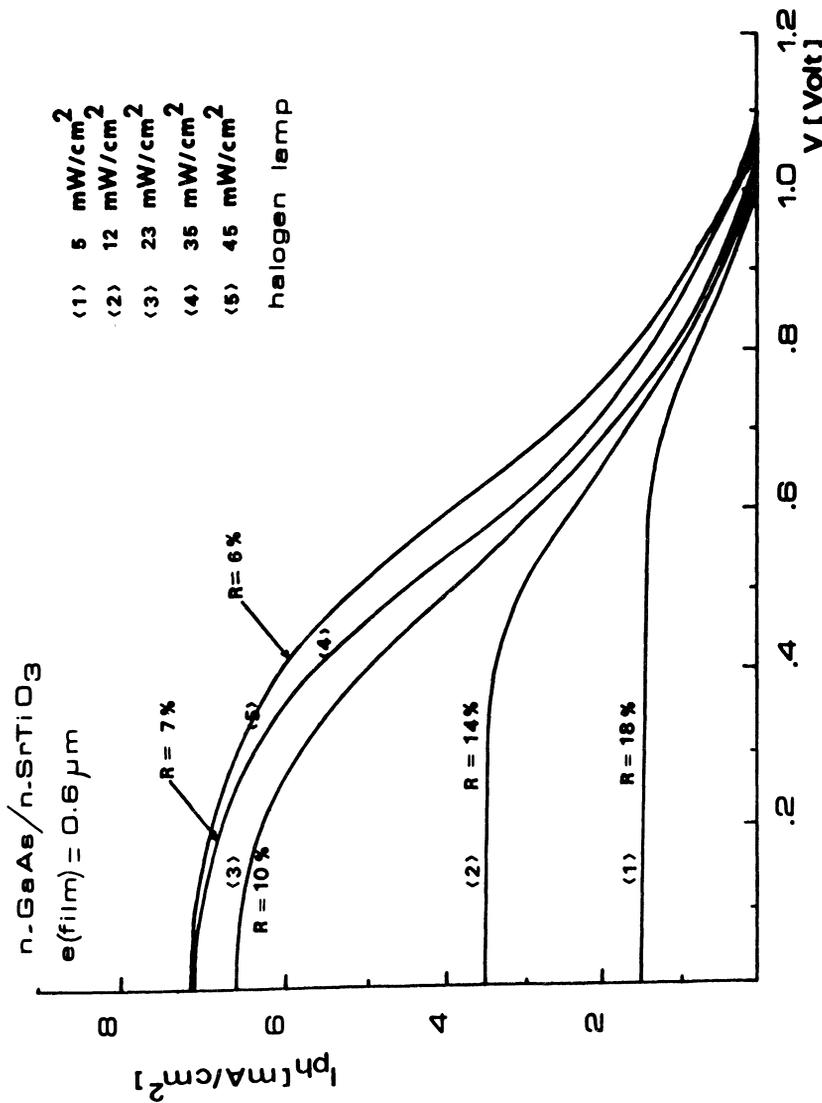


FIGURE 7 Photocurrent vs. potential curves for the n-GaAs/n-SrTiO₃/0.1MIO₃/0.1MI⁻/0.1MKOH/Pt cells.

CONCLUSION

Criteria for picking protective oxide deposits for photo-anodes have been defined on the basis of the most likely and efficient mechanisms of charge transport in the film.

The validity of the strategies adopted here is illustrated by two significant examples.

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