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Transparent conducting oxides as selective filters in thermophotovoltaic devices

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Abstract

Transparent conducting oxides (TCOs) are evaluated as selective filters in thermophotovoltaic (TPV) devices using theoretical considerations. The TCOs plasma frequency and the optical properties in the near infrared are calculated using the Drude theory for free carriers. To improve the radiation transmission for energies higher than the band gap of the cells and the reflection back to the emitter for sub-band gap radiation the TCO's optical properties are studied as a function of electron concentration. Taking into account the photocell and emitter spectral response radiation, the optimal free carrier concentration and the thus thickness of the TCO to be used as selective filter are calculated.

1. Introduction

In a thermophotovoltaic (TPV) system, a heated emitter radiates towards a photovoltaic cell where energies higher than the band-gap energy are converted into electricity. Typical selective emitters are ceramics doped with rare earths, such as ytterbium, holmium and erbium. SiC substrates where either deposited oxides or transition metals like Ta/W are also used. Emitters can exhibit either broadband radiation, compared to near blackbody emission, or selective radiation, emitting in a determinate range of energy. But, in both cases the emitted radiation has to strongly match the band-gap energy of the photovoltaic cell. Up to now radiators, with typical temperature in the range 1500–2000 K, emit at much lower energies and longer wavelengths than 1 μm. In this way, GaSb (with $E_g = 0.72$ eV) and related compounds are suitable to be used for wavelengths up to 1.8 μm and therefore are potential candidates for TPV technology [1, 2]. Ge (0.66 eV) TPV cells with a back-surface mirror have been proposed for emitters radiating between 1400 and 1900 K [3], while the traditional Si (1.1 eV) photovoltaic

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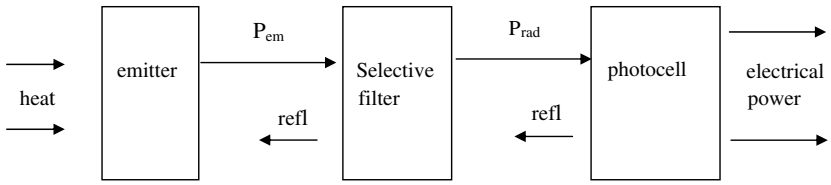

Figure 1. TPV system schematic representation illustrating heat transfer and conversion energy in a TPV system.

cell is limited below 1.1 μm with poor spectral matching with the source radiation. However, Si is available in large quantities with relatively low cost, being a non-toxic material; it has been proposed for TPV prototype systems using a rare earth selective emitter [4].

The problem of the band-gap energy and emitter selectivity matching can be overloaded with the use of a selective filter. In figure 1 a schematic representation, illustrating heat transfer and conversion energy in a TPV system, is shown.

For TPV systems, electrical efficiencies above the 2% experimentally reported [4], using a stable and uniform emitter at the design temperature, are mandatory. To achieve this with the use of a selective filter two important points are to be considered in the TPV design:

(i) the radiation energy below the cell band-gap energy must be reflected to the heated emitter, helping thus to maintain its temperature;
(ii) high transmittance for energies above the band-gap energy is necessary.

Transparent conducting oxides (TCOs) have been reported for this purpose as fitting the above requirements.

Advantages of the TCOs as selective filters are their stability in the temperature range used in TPV applications, and the possibility to prepare them as thin films by different growth methods with high quality and suitable low cost production. But more important is the fact that the optical characteristics of the TCOs can be fitted to TPV device requirements by varying the TCOs' electrical parameters N and μ, where μ is the mobility and N the electron carrier concentration. To do this it is necessary to consider the plasma frequency (ω_p), which is a function of N, due to its key importance in the transparency and reflectivity properties of TCOs.

Having the previous considerations in mind, in this work a computer program has been developed to simulate the TCOs' transmission and reflection spectra with free carrier concentration and layer thickness as variable parameters. The study is applied to Si, GaSb and Ge, which have been proposed, in combinations with several emitters, as photovoltaic materials in TPV systems. The internal quantum efficiency of the photocell, the radiation spectra of the emitter and the electrical–optical properties of the TCOs are considered for simulations. The optimal free electron concentration and layer thickness of the TCOs was calculated, optimizing the optical characteristics of the TCO suitable to be used in each case.

In this work a theoretical study about the use of TCOs as selective filters in TPV systems, grown onto quartz substrates, is presented.

2. Theoretical considerations

To increase the selectivity of the TPV system, selective filters with high transmittance for energies higher than the absorber band-gap energy, and high reflectance for energies lower than the band-gap energy, are required.

Table 1. Summary of coefficients used in equations (4) and (5). (n and k correspond to TCO film and n_0 is the refractive index of the substrate.)

$A = (n^2 + k^2 + 1)(n^2 + k^2 + n_0^2) - 4n^2 n_0$	$B = 2n[n_0(n^2 + k^2 + 1) - (n^2 + k^2 + n_0^2)]$
$C = (n^2 + k^2 - 1)(n^2 + k^2 - n_0^2) + 4k^2 n_0$	$D = 2k[n_0(n^2 + k^2 - 1) - (n^2 + k^2 - n_0^2)]$
$E = (n^2 + k^2 + 1)(n^2 + k^2 + n_0^2) + 4n^2 n_0$	$F = 2n[n_0(n^2 + k^2 + 1) - (n^2 + k^2 + n_0^2)]$
$G = (n^2 + k^2 - 1)(n^2 + k^2 - n_0^2) - 4k^2 n_0$	$H = 2k[n_0(n^2 + k^2 - 1) + (n^2 + k^2 - n_0^2)]$

Reflectivity (R) and transmittance (T) can be evaluated using the following equations, as has been reported in [5]:

$$R = \frac{A\cosh\alpha + B\sinh\alpha - C\cos\xi + D\sin\xi}{E\cosh\alpha + F\sinh\alpha - G\cos\xi + H\sin\xi} \tag{1}$$

$$T = \frac{8n_0\left(n^2 - k^2\right)}{E\cosh\alpha + F\sinh\alpha - G\cos\xi + H\sin\xi} \tag{2}$$

where $\alpha = 4\pi kd/\lambda$, $\xi = 4\pi nd/\lambda$, d is the layer thickness and n_0 the substrate refractive index. In these equations, the refractive index of the incidence medium is assumed to be unity.

Coefficients from A to H, summarized in table 1, are sums of the refractive index and extinction factor of substrate and film.

To evaluate these equations it is necessary to know the refractive index (n) and the extinction coefficient (k), which can be calculated from

$$n = \sqrt{\frac{\varepsilon_1}{2} + \frac{1}{2}\sqrt{\varepsilon_1^2 + \varepsilon_2^2}} \qquad \text{and} \qquad k = \sqrt{\frac{1}{2}\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \frac{\varepsilon_1}{2}} \tag{3}$$

where

$$\varepsilon_1 = \varepsilon_\infty\left(1 - \frac{\omega_p^2}{\omega^2 + \omega_\tau^2}\right), \qquad \varepsilon_2 = \frac{\varepsilon_\infty\omega_p^2\omega_\tau}{\omega(\omega^2 + \omega_\tau^2)}$$

are the real and imaginary parts of the dielectric constant as a function of the frequency in the Drude model:

$$\varepsilon(\omega) = \varepsilon_\infty\left[1 - \left(\frac{\omega_p}{\omega}\right)^2\frac{1}{1 + \left(\frac{i}{\omega\tau}\right)}\right] = \varepsilon_1 + i\varepsilon_2. \tag{4}$$

Here $\omega_\tau = \frac{1}{\tau}$, and τ is the electron scattering time ($\tau = [m^*/q]\mu$ and μ the electron mobility). ω_p is the plasma frequency in a solid, which is a well-known parameter and can be calculated by applying the Drude theory for free carriers, as

$$\omega_p = \left(\frac{4\pi Nq}{\varepsilon_\infty m^*}\right)^{\frac{1}{2}} \tag{5}$$

where N is the conducting electron concentration, q the electron charge, ε_∞ the high frequency dielectric constant, and m^* the electron effective mass.

Summarizing, if the electrical parameters of the TCOs (N, μ) are known, it is possible to evaluate ω_p by using equation (5), from this n and k with the use of equations (4) and (3), and finally the desired R and T spectra using equations (2) and (1).

3. Evaluation of TCOs as selective filters in TPV systems

The free electron concentration (N) is the parameter suitable to be varied by several orders of magnitude in TCOs. This parameter can be varied by doping or modifying stoichiometry of

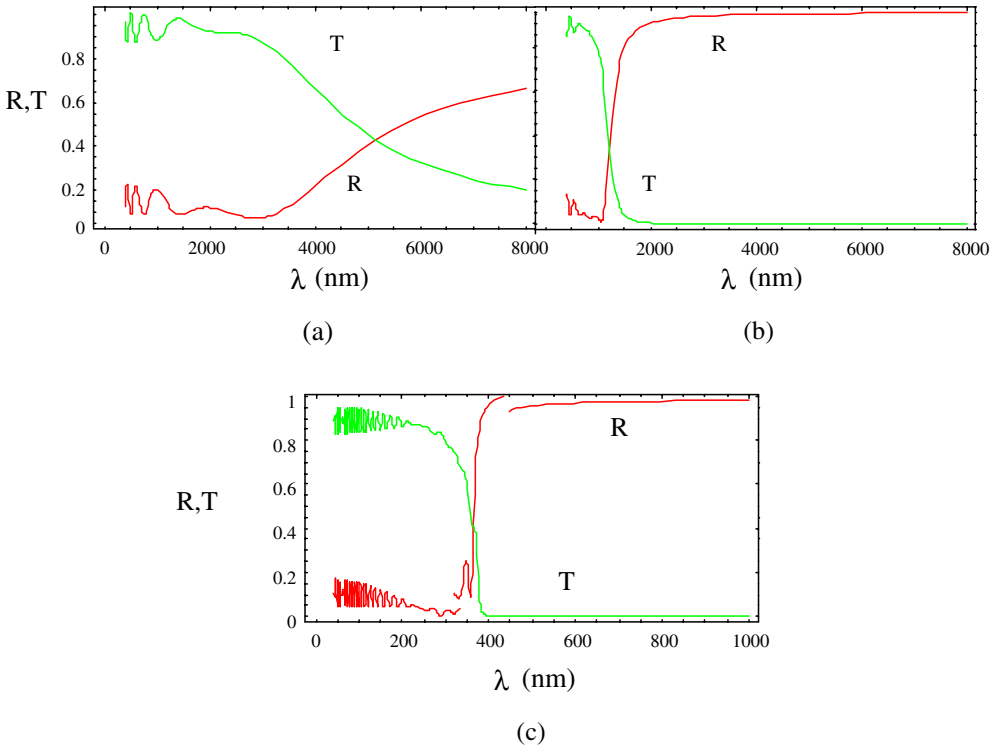

Figure 2. Calculated reflectance and transmittance for different electron concentrations: $N = 7 \times 10^{19}$ cm^{-3}, (b) $N = 7 \times 10^{20}$ cm^{-3} and (c) $N = 7 \times 10^{21}$ cm^{-3}.
(This figure is in colour only in the electronic version)

Table 2. Free electron concentration values (N) measured in different TCOs, grown by several techniques.

N (cm^{-3})	TCO	Reference
7×10^{19}–7×10^{20}	SnO_2:F	[4, 6]
3×10^{20}–8×10^{20}	CdO:F	[7]
1.5×10^{19}–3.6×10^{20}	CdO	[8, 9]
2×10^{17}–1×10^{20}	ZnO	[10, 11]
4.7×10^{20}–3.3×10^{21}	ZnO:Al	[11, 14]
3×10^{18}–7.5×10^{21}	ITO	[15, 16]

the TCO. Of these, the doping method is the most commonly used. In literature the growth of several TCO thin film systems has been reported [4, 6–11, 14–16]. Electron concentration values reported for these TCO thin films are in the range 7×10^{19}–7.5×10^{21} cm^{-3}. Table 2 lists the values of electron concentration obtained for different TCOs as reported in the literature.

As has been established in the theory statement of the problem (section 2), the reflectance and transmittance spectra of SnO_2:F thin TCO films deposited on quartz can be calculated from the spectral dependence of n and k, using the expressions (1) and (2) for different electron concentrations. Results are shown in figure 2, where the reflectance and transmittance behaviour in the near infrared region can be observed. These curves are typical for a TCO, i.e. on increasing the wavelength the transmittance decreases, while the reflectance increases.

The crossover point between reflectivity and transmittance shifts to shorter wavelengths when N is increased. Due to these facts and for the evaluation of the best performance of the TCO under consideration in each case, it is necessary to define a figure of merit. The following figures of merit have been used in this work:

$$Q_1 = \frac{\int_{\lambda=0}^{\lambda_{gap}} \mathrm{SR}(\lambda)\mathrm{QE}(\lambda)T(\lambda)\,\mathrm{d}\lambda}{\int_{\lambda=0}^{\lambda_{gap}} \mathrm{SR}(\lambda)\mathrm{QE}(\lambda)\,\mathrm{d}\lambda} \tag{6}$$

where $\mathrm{SR}(\lambda)$ is the spectral response of the emitter, $\mathrm{QE}(\lambda)$ the internal quantum efficiency of the photocell and $T(\lambda)$ the transmittance spectra of the TCO. The maximum value of Q_1 optimizes the transmittance properties of the TCO in the system when $\lambda \leqslant \lambda_{gap}$.

On the other hand, it is necessary to take into account the back radiation towards the emitter. The energy emitted is $\mathrm{SR}(\lambda) = AH(\lambda)$, where A represents the absorbance power of the emitter at thermal equilibrium and $H(\lambda)$ is the incident radiation. With this in mind we calculate the back reflection to the emitter as:

$$Q_2 = \frac{\int_{\lambda=\lambda_{gap}}^{\infty} AH(\lambda)R(\lambda)\,\mathrm{d}\lambda}{\int_{\lambda=\lambda_{gap}}^{\infty} AH(\lambda)\,\mathrm{d}\lambda} = \frac{\int_{\lambda=\lambda_{gap}}^{\infty} SR(\lambda)R(\lambda)\,\mathrm{d}\lambda}{\int_{\lambda=\lambda_{gap}}^{\infty} SR(\lambda)\,\mathrm{d}\lambda} \tag{7}$$

where $R(\lambda)$ is the reflectance spectrum of the TCO for sub-band-gap energy energies of the photocell. The maximum value of Q_2 optimizes the reflection properties of the TCO in the system for $\lambda \geqslant \lambda_{gap}$. The best performance of the TCO is then obtained for the maximum of the figure of merit Q, defined as

$$Q = Q_1 \cdot Q_2.$$

3.1. TCOs as selective filters for a silicon based TPV system

SnO_2:F, with an electron concentration of 7×10^{20} cm^{-3}, an electron mobility of 17.8 cm^2 V^{-1} s^{-1}, a layer thickness of 468 nm and a transmittance of 76% at the maximum emitter (Yb_2O_3) radiation, has been recently reported as a selective filter in a Si based TPV system, exhibiting an electricity-to-gas (heat source) power efficiency of 2.1% [4].

We have simulated this system, Yb_2O_3/TCO/Si, and the results are shown in figure 3, where there can be seen the variation of Q_1, Q_2 and Q as a function of the free electron concentration of the TCO. The maximum of Q corresponds to an optimal electron concentration ($N = 8.7 \times 10^{20}$ cm^{-3}) for the TCO used like a selective filter in the silicon based TPV devices. This value fits quite well with experimental ones, 7×10^{20} cm^{-3}, reported for SnO_2:F used like a selective filter [4]. However, in that work, the authors found that the efficiency of the system using SnO_2:F like a selective filter was lower (2.1%) than the efficiency using the quartz filter (2.4%). The authors attributed this difference in efficiency to the transmission loss in the SnO_2:F filter. For this reason, we have also calculated the Q parameter as a function of the layer thickness in the 100–600 nm range for a fixed value of the electron concentration of the SnO_2:F thin TCO films. These calculations are shown in figure 3. In this figure one can observe that the absolute maximum of $Q = 0.654$ is obtained for a thickness $d = 230$ nm. The thin film thickness in [4] is $d = 468$ nm, which following our calculations corresponds to a value of $Q = 0.606$.

3.2. TCOs as selective filters for GaSb and Ge based TPV systems

Following the same procedure we have calculated the absolute maximum Q values for Yb_2O_3/TCO/Ge and Yb_2O_3/TCO/GaSb systems, considering the internal quantum efficiency for both systems reported in the literature [3, 17] respectively. In figure 4 we have also

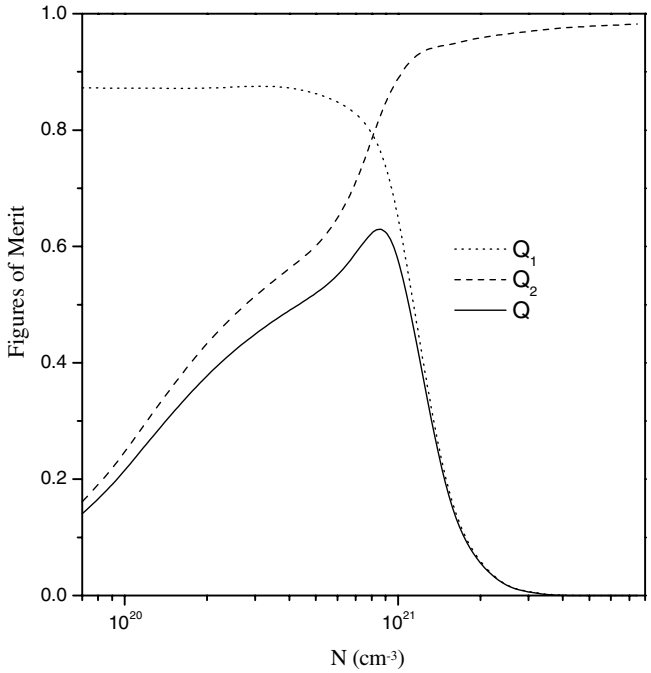

Figure 3. Q_1 (· · · · · ·), Q_2 (- - - -) and Q (full line) variation as a function of the electron concentration for the TCO/Si system. These values were obtained taking $d = 230$ nm and $m^* = 0.4\ m_0$.

Table 3. Maximum Q values, optimal layer thickness, d, and electron concentrations N for the TCO/Si, TCO/GaSb and TCO/Ge based TPV systems. The possible TCOs matching these characteristics can be selected from the results of table 2.

TPV system	Q	d (nm)	N (cm^{-3})	η
Yb_2O_3/TCO/Si homojunction	0.65	238	8.7×10^{20}	0.27
Yb_2O_3/TCO/GaSb homojunction	0.73	312	4×10^{20}	0.53
Yb_2O_3/TCO/Ge	0.75	302	4×10^{20}	0.56

shown the results for calculations regarding this system, while in table 3 we report the optimal conditions for the use of TCOs as selective filters in the three systems studied in this work. As can be observed, the highest value for the Q parameter is obtained for the Yb_2O_3/TCO/Ge system, followed by Yb_2O_3/TCO/GaSb and Yb_2O_3/TCO/Si. In consequence, and according to our results, the efficiency of the Si based system could be improved using SnO_2:F with $N = 8.7 \times 10^{20}$ cm^{-3} and a layer thickness of 238 nm, instead of 468 nm.

On the other hand, for increasing the energy conversion efficiency, the spectral response of the photovoltaic cell needs to be adapted to the radiation spectra of the emitter. In this way, the selectivity (η) evaluates the coupling between the spectral response of the photovoltaic cell and the radiation spectra of the emitter, and is defined as the radiation power integrated over photon energies above the absorber band-gap energy, relative to the total radiation power of the emitter. Selectivity is frequently used as an estimation of the spectral coupling of the TPV system. The values for selectivity of Yb_2O_3 emitter with respect to the Si, GaSb and Ge photovoltaic cells have been included in table 3. Considering that the calculated value of the

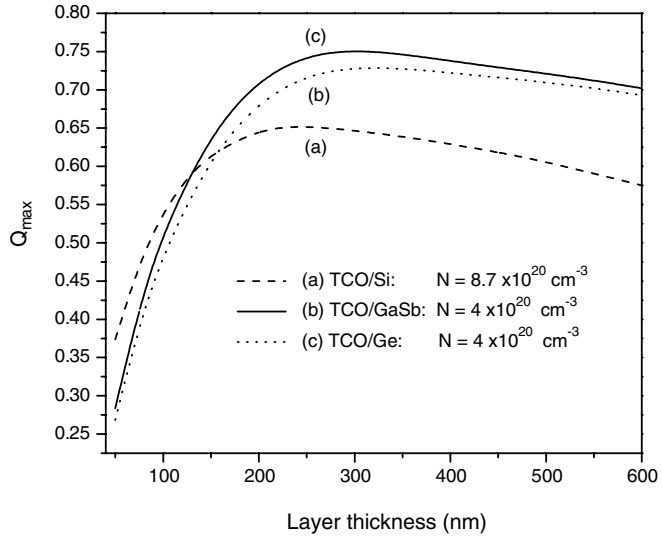

Figure 4. Calculated absolute Q_{max} for: TCO/Si system, with $N = 8.7 \times 10^{20}$ cm^{-3} (a); TCO/GaSb system with $N = 4 \times 10^{20}$ cm^{-3} (b); and TCO/Ge: system with $N = 4 \times 10^{20}$ cm^{-3} (c).

Q parameter takes into account the emitter radiation and the spectral response of the photocell, Q can be considered as an estimate of the selectivity when transmittance and reflectance of the selective filter are involved. In fact, table 3 shows that Q has the same tendency as η. In consequence, the figure of merit Q is a better characterization of the spectral coupling of the TPV system (including the TCOs selective filter) than the selectivity η.

4. Conclusions

TCOs as selective filters for TPV systems have been computer designed and tested. Parameters of the TCO, i.e. optimal thicknesses and free electron concentrations, were determined for Si, GaSb and Ge photocell based TPV systems. The application of our calculation in the case of the record efficiency of silicon solar cell based TPV system shows that the optimal electron concentration is near to the ones used in this work, while the efficiency could be improved using a TCO layer thickness of 268 nm instead of 468 nm reported by the authors of [4]. In general, it has been demonstrated that the use of a TCO as a selective filter, with adequate values of electron carrier concentration and thickness layer, is an alternative for the improvement of the efficiency in TPV systems.

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