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PHOTOCURRENT SPECTROSCOPY APPLIED TO SEMICONDUCTOR THIN FILMS: CDS

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RESUMEN

En este trabajo se presenta el resultado de la aplicación de la técnica de fotocorriente espectral en el análisis cuantitativo de semiconductores, en el caso especifico de películas de sulfuro de cadmio (CdS). Se presentan tres modalidades de medición, cuyos resultados son en si complementarios y confirman, que los niveles de energía más relevantes en CdS, desde el punto de vista fotoeléctrico, corresponden a los valores: 2,0; 2,26; 2,38; 2,47 y 2,60 eV

ABSTRACT

In this work, we present results of spectral photocurrent measurements in the quantitative diagnostic of semiconductors, in the specific case of cadmium sulfide (CdS) thin films. We present three measurement modalities. The results are each other complementary and confirms, that the most relevant energy levels in CdS, from the photoelectric point of view, correspond to the values: 2,0; 2,26; 2,38; 2,47 and 2,60 eV

INTRODUCCIÓN

The subject of solar cells is nowadays at world-wide level, one of the most important applications in the field of semiconductors, due essentially to its increasing relevance like alternative power source. The present investigations are mainly directed to the development of new materials and also of new techniques of processing, so that sophistication and elaboration costs are reduced substantially, what would allow a massive diffusion of this technology. In connection to this point, we would like to emphasize the work developed by Prof.

Michael Graetzel (University of Swiss Lausanne) [1] on the basis of the TiO2 semiconductor, which is processed from a simple printing technique and activated by organic Dyes, obtaining surprising good results, comparable with the normal standards of conventional solar cells.

One of the basic aspects of mayor interest at the moment, in the optimization of solar cells, constitutes the study of the energy levels that take part in the photovoltaic response of the semiconducting materials [2] and the corresponding electric field generated from their different unions [3]. This parameter define lastly the global photovoltaic efficiency, and classically are studied from the analysis of indirect measurements: Photoluminescence, electrical resistance, IV response, etc. Although, the most direct measurement of this characteristica: the Photocurrent spectroscopy, has been marginalized until nowadays by diverse reasons (apparent non reproductivity, strong dependency of the intensity results on the radiating source, etc). Nevertheless, in the last years a great number of investigators are becoming aware from the advantages of this technique for the analysis of semiconductors and solar cells [4].

One important physical question, about the energy levels involved in a photovoltaic effect, is refereed to the nature of these internal transitions. In each case, it must be cleared, which of the following process is the dominant one and if possible to evaluate its magnitude: *Band-Band transition, Trap or surface state influence, Schottky barrier*.In these sense, we are deep convincing, that the Photocurrent spectroscopy can give us enough information to elucidate very accurately this processes [5].

The present contribution is one step forward to demonstrate the effectiveness of the method of Photocurrent spectroscopy in the quantitative diagnostic of semiconductors. Applying it to the specific case of cadmium sulfide (CdS) thin films. We report here some photocurrent spectra realized on this material in a transversal configuration (EXPERIMENTAL section). The results and convenience of this proceedment will be displayed in the CONCLUSSIONS section.

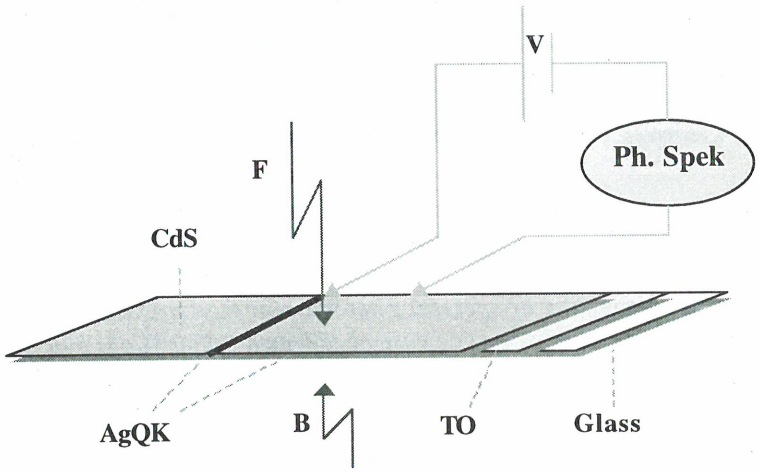

Fig.1 *Schematic overview of a transversal photocurrent array and the disposition of the layers involved : CdS (Cadmium sulfide), TO (Tin oxide).*

EXPERIMENTAL

In this section, we describe the experimental arrangements employed and the corresponding results obtained, in the following order:

Transversal Photocurrent configuration

Photocurrent spectrometer
Result 1: Frontal illumination (F)
Result 2: backward illumination (B)
Result 3: backward illumination (B) plus blending

TRANSVERSAL PHOTOCURRENT CONFIGURATION

In figure 1, we describe schematically the transversal array: Over a Glass substrate, a thin TO (Tin oxide) layer (near 1 μm , 300 Ω•) is deposited by spray pyrolisis, over the TO conducting layer, a cadmium sulfide (CdS) film (near 0,5 μm) is formed by vacuum evaporation. Lastly, over the CdS film, we make two strips of silver printing (AgQK), as electrical contacts. From these contacts, we close a serial circuit with the Photocurrent meter (Ph. Spek). A battery (V) is used to polarize the circuit. If the monochromatic light arrive

direct to the CdS layer, we call this a Frontal (F) illumination. If the light arrive to the CdS layer from the glass side, we call this the backward (B) illumination.

The symmetry of the contacts disposition (Both silver printing) and the illumination zone (centered at CdS) assures a direct response of the CdS material.

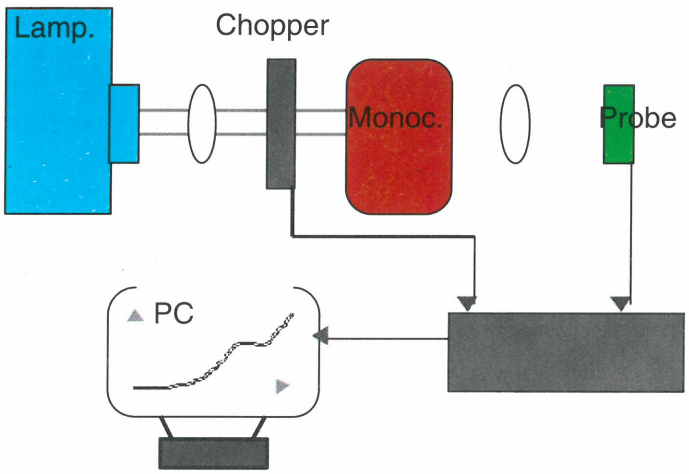

Fig. 2 Experimental setup : Photocurrent spectrometer system

PHOTOCURRENT SPECTROMETER

In figure 2, we describe the experimental setup employed to evaluate Photocurrent spectra: White Light from a Halogen Lamp (600 W), goes through a chopper, into a Monochromator and this finally arrives to the analyzed probe (CdS Layer). The probe response is detected by a Lock-In amplifier and conducted to a PC for recording and processing.

Result 1 : Frontal Illumination (5J2)

Figure 3 shows the result of a transversal photocurrent spectrum, obtained with a CdS layer, when light incide on the frontal side.

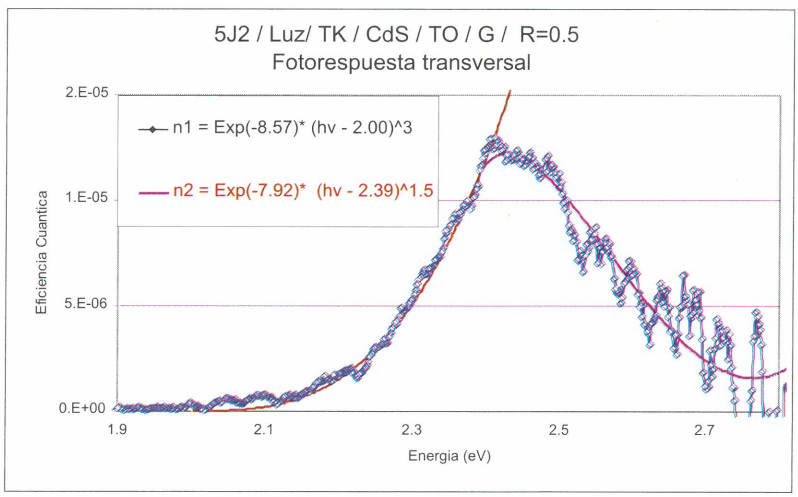

Fig. 3 Quantum efficiency spectrum of the Photoresponse, obtained from a CdS probe (5J2) in a transversal configuration with frontal illumination.

From photoresponse spectrum (figure 3), we can observe a relative strong increase of free charge up nearly 2 eV. This generation is described by the relation n_1 (theoretical fitting / figure 3) and corresponds to a 2,0 eV transition. This free charge increasement take place until nearly 2,4 eV, where it attains its maximum and begin to decrease asymptotically as n_2 (theoretical fitting / figure 3). The energy transition responsible of this decreasement is 2,39 eV.

Discussion To Result 1:

The 2,0 eV transition takes place in the CdS material, at the back side (Interface: CdS / TO) due to a Trap located 2,0 eV over the CdS valence band. Up 2,39 eV (CdS band gap), the frontal absorption do not allow the radiation to arrive at the back side, causing the decreasement of the 2,0 eV signal. fig. 4 shows the energy diagram model from Result 1.

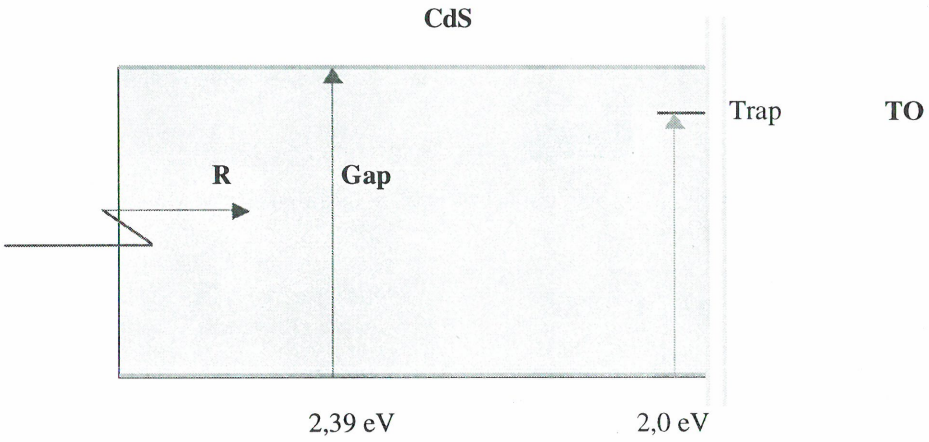

Fig. 4 *Energy band model explaining the photoresponse spectrum 5J2*
R: Radiation sense

The assigned Trap (2,0 eV) lies 0,39 eV below the CdS conduction band and is well probably a localized CdS surface state. It is well known from the literature [6] the occurrence of a bulk trap 0,41 eV below the CdS conduction band. From photo luminescence measurements [7] have been observed also a trap 0,4 eV below the conduction band.

The CdS band-band absorption do not contribute apparently in this case to the photo conduction process, probably due to the distance to the back TO conductive layer, loosing their charge through frontal recombination centers or via trap capture processes.

As a final conclusion of this measurement, we can assume the occurrence and reinforcement of a CdS trap at 0,4 eV , at the Interface between CdS and TO films and the CdS band-band absorption effect.

A complement measurement to this case (5J2) will be treated in the next case 9J2.

Result 2 : Backward Illumination (9J2)

Figure 5 shows the result of a transversal photocurrent spectrum, obtained for a CdS layer, when light incide from the back side.

From photo response spectrum 9J2 (figure 5), we can observe again, the same as in case 5J2, a relative strong increase of free charge up nearly 2,0 eV. This generation is described by the relation n_1 (theoretical fitting / figure 5) and corresponds to a 2,02 eV transition. This free charge increasement take place

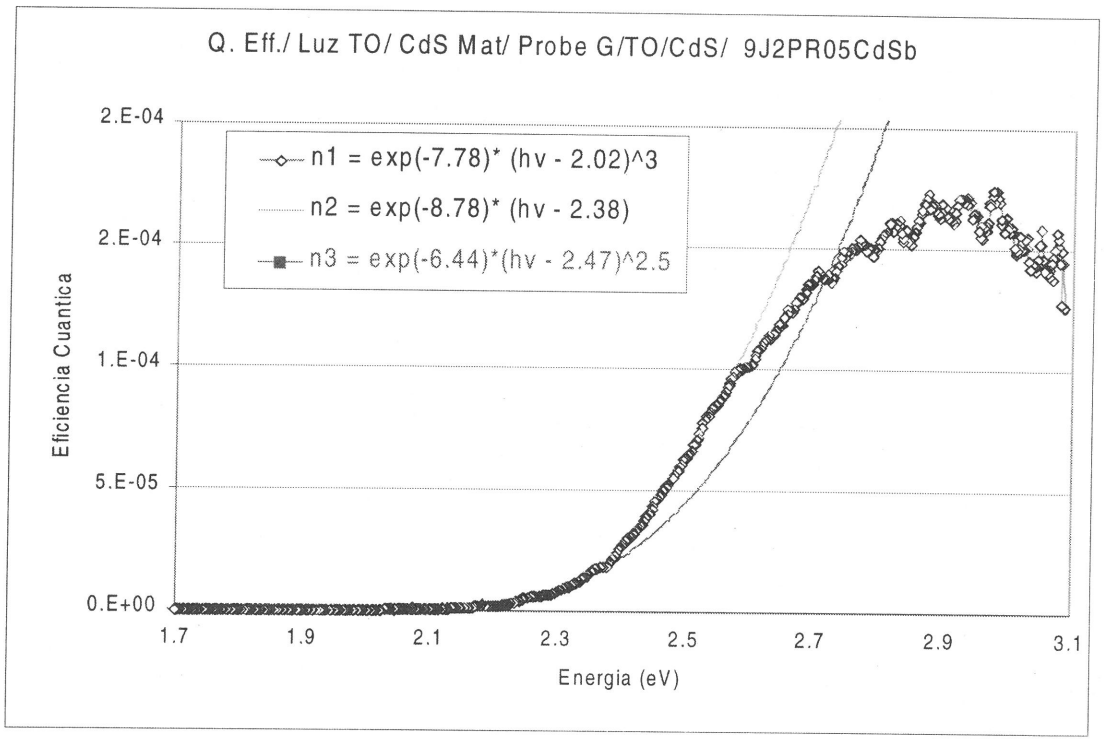

Fig. 5 *Quantum efficiency spectrum of the measured photo response 9J2*

until nearly 2,4 eV, where a new charge generation process begin to contribute. This new contribution is described by n_2 (theoretical fitting / figure 5) and is due to a 2,38 eV transition. Up nearly 2,5 eV, the photocurrent response begin to decrease asymptotically as n_3 (theoretical fitting / figure 5). The energy transition responsible for this decreasement is 2,47 eV.

Discussion to Result 2:

The 2,02 eV transition takes place in the CdS material, at the back side (contact face : CdS / TO)due to a Trap located 2,02 eV over the CdS valence band (essentially the same as in result 1). Up 2,38 eV (CdS band gap) a new charge generation source take place. The radiation is absorbed by band-band transition in CdS, immediately on the interface CdS/TO, allowing an optimal collection of free charge. The decreasement shown up 2,47 eV is well probably due to radiation losses. From the Literature [7] it is well known a luminescence transition of 2,47 eV.

Fig. 6 shows the energy diagram model of result2. The assigned Trap of 2,02 eV (0,36 eV below the CdS conduction band), coincide basically with the 2,0 trap detected in 5J2 and corresponds nearly to the known trap 0,40 eV [6] and is well probably a localized CdS surface state formed at the contact with TO.

In this case, the CdS band-band absorption contribute to the photo conduction process, due to the fact of direct incidence of light onto the CdS/TO junction, confirming the assertions done in case 5J2.

As final conclusions of measurement 9J2, we can resume:

- The occurrence and reinforcement of a CdS trap at 0,36 eV at the common contact between CdS and TO films.
- The production of Band-Band transitions (2,38 eV) in case of backward (TO side) illumination, in contrast to the absorption obtained in case of frontal illumination (Case 5J2).

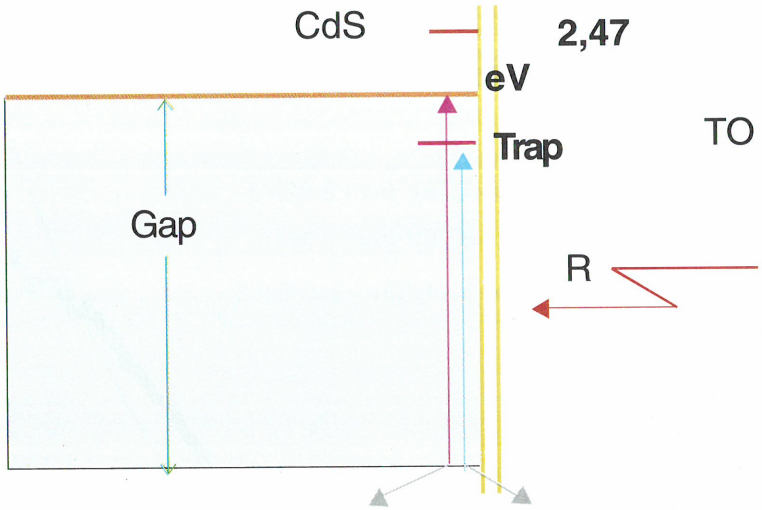

Fig. 6 Energy band model explaining the photoresponse spectrum 9J2

- The occurrence of a energy level (2.47 eV) in CdS, with a net negative contribution to the photocurrentgeneration. This last statement could mean: A) This energy level is just a limit zone of the absorption band. B) This energy level is involved in a reemission or radiation less process. C) This energy level correspond to a photovoltaic effect produced in the contact zone (Ag silver paste) when light incomes into it.

  In order to discard possibility (C), we repeated measurement 9J2, but changing the polarization of voltage source (V / Fig.1), obtaining this time a positive contribution of the 2,47 eV energy level. Confirming this way, the fact of a photovoltaic contribution from the contacts (possibility C).

To confirm the results obtained with measurement 9J2, we realized a new measurement (15F2), taking in count, the incorporation of blend shutters (B) in the probe array (fig 7).

In spite of the results obtained in measurement 9J2, we realized a new one (15F2), taking in count the addition of two screens (B, figure 7), in order to assure that incoming light, incide only in the CdS free zone.

Result 3 : Backward illumination II (15F2)

CdS: CdS Film
TO: Tin Oxide Film
G : Glass substrate
V : Voltage polarization
I : Photocurrent
R : Radiation
B : Screen
Agp: Silver paste contact

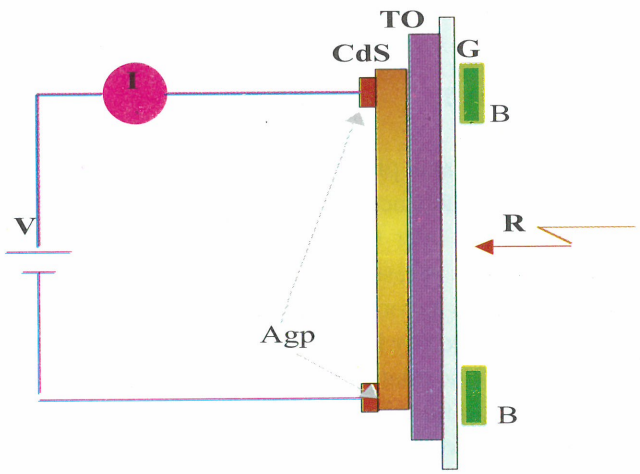

Fig. 7 Schematic view of the probe disposition in measurement 15F2.

Figure 8 shows the resulting photoresponse spectrum (15F2). We observe again, as in previews spectra, positive contributions to the photocurrent response, which are due to transitions that liberate free charge carriers, that participate in the photocurrent process. This we will refer as "constructive transitions". There are also negative contributions to the photocurrent, due mainly to transitions, that don't contribute to the total photocurrent process. This we will refer as "destructive transitions".

Our experimental results in the case 15F2 will be shown in the Table I. The data are arranged according to the transition energy involved. We indicate also the type of transition (constructive, destructive), the type of suspected level energy involved (trap, Luminescence state) and the most probable correspondence with known levels (Reference).

The individual contributions to the total quantum efficiency response are described by the relations n_1, n_2, n_3, n_4 (theoretical fitting / figure 8).

As stated before, Measurement 15F2 is essentially the same as 9J2, except that in this case the contact zones in CdS, are covered to the incoming light (Blending B / Figure 7). As in measurements 5J2 and 9J2, the 2,0 eV transition takes also place. This was explained to occur, in the CdS material, at the back side (contact face : CdS / TO) due to a Trap located 0,38 eV under

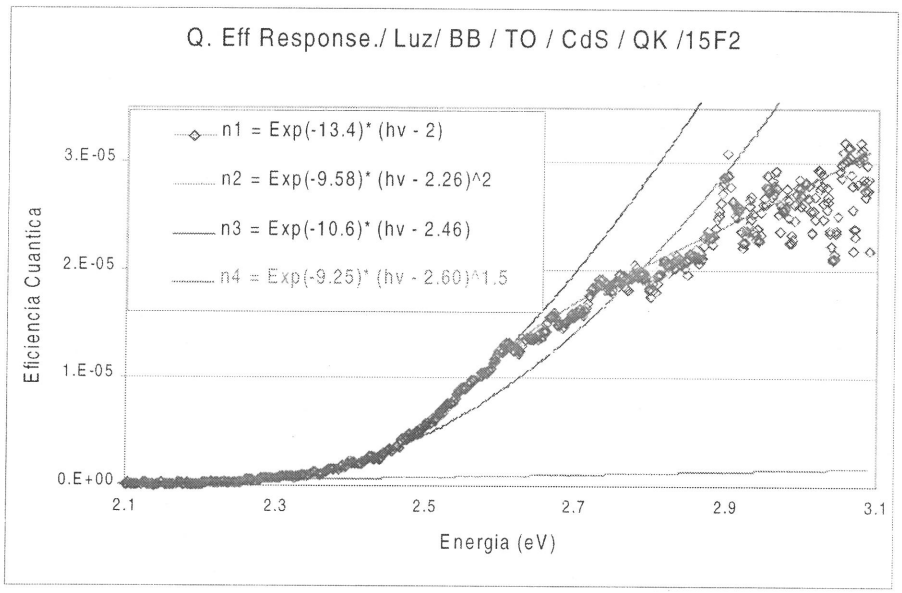

Fig. 8 Quantum efficiency spectrum of the measured photoresponse 15F2

Table I: 15F2

Contribution	Transition/ Energy (eV)	Transition/ Type	Level/ Type (eV)	Reference (eV)
1	2,00 eV	Constructive	0,38 : Trap	0,40 [6]
2	2,26 eV	Constructive	0,12 : Trap	0,14 [6]
3	2,46 eV	Constructive	2,46 : L* State	2,47 [7]
4	2,60 eV	Destructive	2,60 : L* State	2,55 [7]

the CdS conduction band.

Up nearly 2,3eV, a new charge generation process begin to evolve. This new contribution is described by n_2 (theoretical fitting / figure 8) and is caused by a 2,26 eV transition. This signal was not seen in the 9J2 measurement probably due to the preponderance of the 2,38 eV contribution. The 2,26 contribution corresponds to the transition of a level trap located 0,12 eV under the CdS conduction band and must be assigned to the known trap level of 0,14 eV [6]. Fig. 9 show the energy band model.

Up nearly 2,46 eV, the photocurrent response begin to increase again as n_3 (theoretical fitting / figure 8). In case 9J2, we obtained also a similar contribution

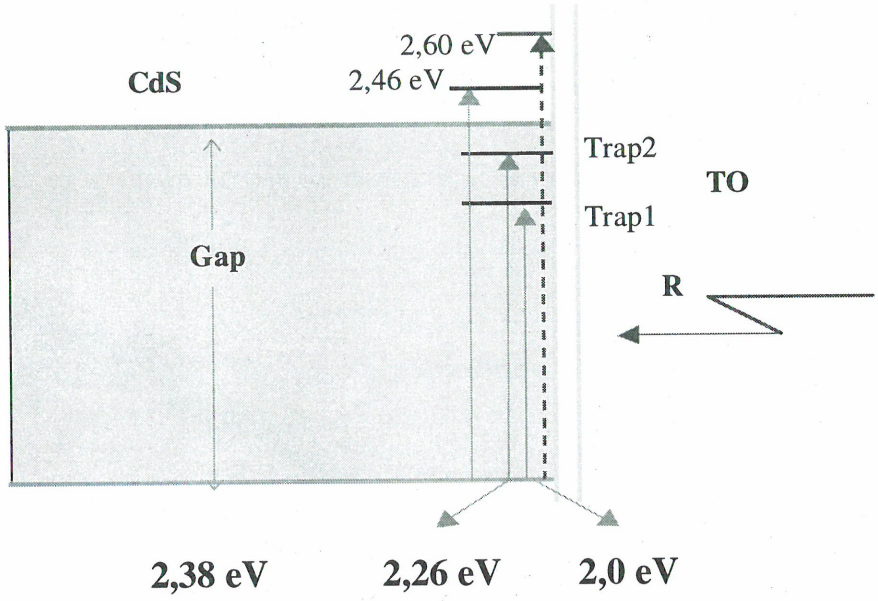

Fig. 9 Energy band model explaining the photoresponse spectrum 15F2

(2,47 eV), although it was a negative one. This was interpreted to be caused by a photovoltaic effect in the contacts. This last statement was actually confirmed by direct PV measurements and will be publicized next. As in case 9J2, the 2,46 eV is associated to a well known luminescent state (2,47 eV , [7])

Up 2,60 eV, a continue decreasement in the quantum efficiency take place. This can be understood as due to a decreasement in the absorption strength (Border of the conduction Band). This is in concordance with own transmission spectra measurements, where, CdS films shows also a transmittance increasement below 470 nm. In the Literature, there are no mention to this 2,6 eV state.

Nevertheless, there are reported luminescent states in the range 2,55 eV to 2,38 eV [7], which is also an indication of the limitation of the CdS conduction band.

CONCLUSIONS

As conclusions of this measurements, we can mention:

- The occurrence and reinforcement of a CdS trap at 0,38 eV at the common contact between CdS and TO films.
- The occurrence of a CdS trap at 0,12 eV at the common contact between CdS and TO films.
- The disappearing of the 2,38 eV contribution from spectrum 15F2 is again a indication of a photovoltaic behavior of the contacts.
- The occurrence of a energy level (2,46 eV) in CdS,

as in case 9J2, which contributes constructively to the photocurrent, producing charge generation.

- The presence of a energy level (2,60 eV) in CdS, which contribute negative to the total photocurrent and means probably, the fallout of the absorption coefficient.
- In transversal photocurrent measurements, it is very important to cover the electric contacts to avoid additional effects (per example : photovoltaic signals).

As a final conclusion, we would like to remark the following:

- Photocurrent spectra analysis made at this work allowed the quantitative determination and influence of certain energy levels in the photoresponse of CdS. The results are consistent and reproductively. This is a step forward, to prove the great effectiveness of the method in the study of semiconductors.

ACKNOWLEDGMENT

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