PHOTOCURRENT SPECTROSCOPY APPLIED TO THIN FILM SOLAR CELLS BASED ON HYDROGENATED AMORPHOUS SILICON (A – SI:H)

ESPECTROSCOPIA DE FOTOCORRIENTE APLICADO A CELDAS SOLARES DE PELICULA DELGADA ELABORADAS EN BASE A SILICIO AMORFO HIDROGENADO (A – SI:H)

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ABSTRACT

Using photocurrent spectroscopy, we report measurements of the photo response below the optical gap in hydrogenated amorphous silicon (a-Si:H). The a-Si:H films were grown in a non conventional DC plasma assisted discharge chamber. The measurements suggest that the density of states of this material is not very different than conventional intrinsic a-Si:H (device-quality) and not so extended as usually taken. The positions of the corresponding photovoltaic transition energies are determined and agree very well with known data obtained by other methods.

Key works: *Thin films, Amorphous silicon, Photocurrent measurements, Solar cells.*

RESUMEN

En este trabajo reportamos mediciones de la respuesta óptica de silicio amorfo (a-Si:H), bajo el umbral del Gap óptico, empleando el método de espectroscopia de fotocorriente, Las películas de a-Si:H fueron elaborados por medio de un sistema plasmático DC no convencional. Las medidas sugieren que la densidad de estados de este material no es muy diferente del silicio amorfo convencional. Se determinan las posiciones de las correspondientes transiciones electrónicas fotovoltaicas, existiendo una buena correspondencia con niveles internos conocidos del material.

Palabras clave: *Película delgada, Silicio amorfo, Medidas de fotocorriente, Celdas solares.*

INTRODUCTION

Due to the interest in its basic physics and many possible applications, hydrogenated amorphous silicon (a-Si:H) has been intensively studied in the last twenty years [1, 2], though the distribution of the defect states in the energy gap is still the subject of considerable controversy [3]. Because of the critical effect of the defect states on the transport properties and recombination kinetics in this material, many of the studies were focused on determining the energy distribution of these states. Correspondingly, quite a few experimental methods, which have been previously used for crystalline semiconductors, were extended to suit studies of a-Si:H.

The prominent techniques [4, 5] have been: field effect, deep level transient spectroscopy, photovoltage deflection spectroscopy (PDS), and the constant photocurrent method (CPM). For the most studied and best understood material: undoped a-Si:H, only the later two techniques have been shown to yield reliable information. The most important drawback of these two methods is their analysis and the interpretation of the data to which

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Numerous papers [6, 7] have been devoted.

This is because deconvolution of the observed spectra requires some assumptions, the applicability of which is, at least a priori, questionable for a-Si:H and the results of which can lead to different conclusions. In particular, the contribution of both charge carriers to the photoconductivity in the CPM does not allow to distinguish between excited electronic transitions from the valence band to a localized state and transitions from a localized state to the conduction band.

On the other hand, nevertheless original photocurrent measurements, were denied in favor of the CPM method. The work done by our group [8, 9, 10] in the last years in relation to a direct application of photocurrent measurements to study photovoltaic materials have induced us to applied it to a-Si:H and its metal contacts. It is the purpose of this letter to show that conventional photocurrent measurements can also be applied with success to materials like a-Si:H.

REVIEW

Before presenting our results, we give a brief review of the previous work relevant to a-Si:H:

- It is generally believed that in a-Si:H, there is one dominant point defect (commonly referred to as a dangling bond, a site which the silicon is threefold-coordinated), which exists [11] in three charge states, D^+, D^0, D^- Although other defects, such as residual impurities, can exist in a-Si:H, the silicon dangling-bond defect is all that is necessary to explain the vast majority of the experimental data in intrinsic a-Si:H (device-quality material). These localized states are broad (nearly 0.6 eV) and centered at: 0.8 eV (D^-), 1.1 eV (D^0) and 1.5 eV (D^+), from the valence band as described by Schumm (defect pool model) [12].

- Proton nuclear magnetic resonance (H NMR) studies [13] have provided direct evidence of two separate hydrogen phases, a dilute phase and a clustered phase. For device quality films, hydrogen binds to the silicon network as monohydrides (Si-H) and the clustered phase constitutes half or more of the H atoms. Isolated and clustered hydrogen evolved by a thermally activated process with an activation energy of 2.1 eV and 1.4 eV, respectively.

- Surface photovoltage spectroscopy (SPS) is used [14] to determine the position of the deep defect state levels in intrinsic hydrogenated amorphous silicon (a-Si:H). The basic results of these measurements are the identification of the principal states throughout the band gap of a-Si:H (device quality):

  - Valence band to localized state transitions: 1.1-1.2 eV, 1.66-1.70 eV, (1.26 eV)*,
  - Localized state to conduction band transitions: 0.86-0.90 eV, 1.40-1.45 eV,
  - The data (*) were found when using stainless steel as substrate for a-Si:H

- Schottky Barriers based on a-Si:H are used extensively to study the optoelectronic properties of intrinsic a-Si:H self [15]. In a recent work done by Al-Dhafiri [16] on Au/ a-Si:H junctions, the barrier height was determined among other parameters. They report a value of 0.492 eV for the untreated (no annealing) contact Au/ a-Si:H.

- Luminescence peaks from ion-beam treated a-Si:H were identified optically [17] with energies lying in the range from 0.7 eV and 0.95 eV, which were associated to two groups of gap states with thermal activation energy of 0.71 eV and 0.84 eV.

- Photoexcitations in a-Si:H have been studied by techniques of photoinduced absorption (PA), detecting among others, a localized state 0.35 eV below the conduction band [18]

Fig. 1, resumes the data (localized energy levels) found from the literature for a –Si:H.

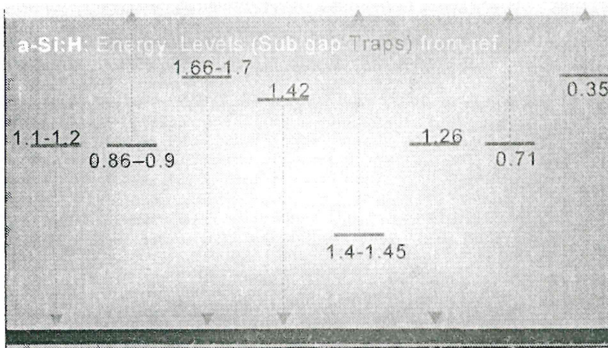

Fig. 1 Localized energy levels (Trap states) in the band gap of a- Si:H, taken von the references [11, 12, 13, 14, 15, 16, 17].

EXPERIMENTAL

Sample preparation

Samples of a-Si:H were grown on different substrates (roughened glass, tin oxide coated glass, metal folia: aluminum, stainless steel, copper) by a non conventional DC plasma deposition system Fig. 2. A hydrogen DC plasma (500 mtorr) is maintained between 2 planar electrodes, over the bottom electrode Silicon (Lump) brockets are spread and the substrates are fixed at the upper electrode. The plasma attacks the silicon crystals and produce hydrates (i.e. silane), which reacts and forms at the substrate zone (upper side) a-Si:H films.

Tin oxide films were deposited on glass substrates by a conventional pyrolisis spray technique. Metal contacts (Au, Ag, Al, etc.) were obtained by vacuum evaporation.

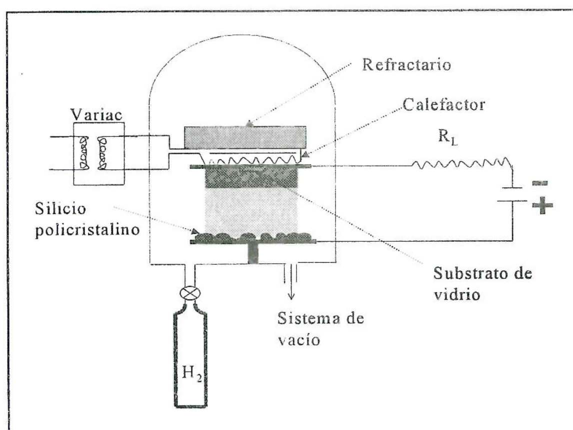

Fig. 2 DC Glow discharge system UNI, used to elaborate a-Si:H thin films.

Photocurrent measurements

In Fig. 3, 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 (a-Si:H Layer). The probe response is detected by a Lock-In amplifier and conducted to a PC for recording and processing.

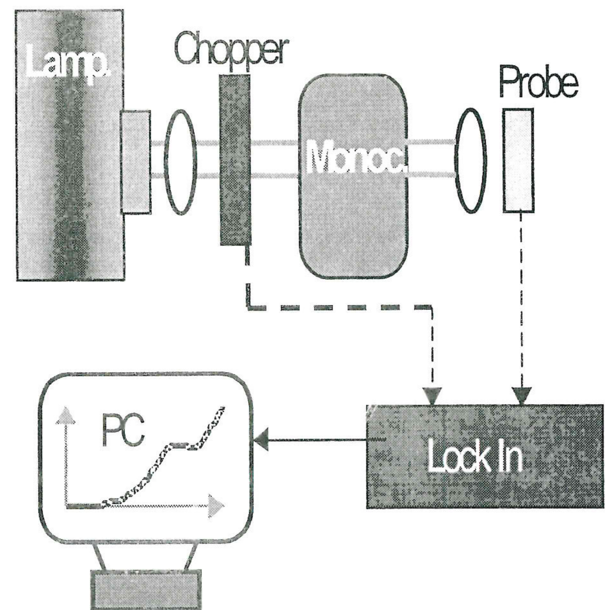

Fig. 3 Experimental setup: Photocurrent spectrometer system.

In the next section, we describe the experimental arrangements employed, in the following order:

a) Transversal Photocurrent configuration
b) Photovoltaic response

Transversal photocurrent configuration

In Fig. 4, we describe schematically the transversal array: Over a Glass substrate, a thin TO (Tin oxide) layer (near 1 μm , 300 $\Omega_{\square}$) is deposited by spray pyrolisis, over the TO conducting layer, a a – Si:H film (near 1 μm thick) is formed by DC Glow discharge. Lastly, over the a – Si:H 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.

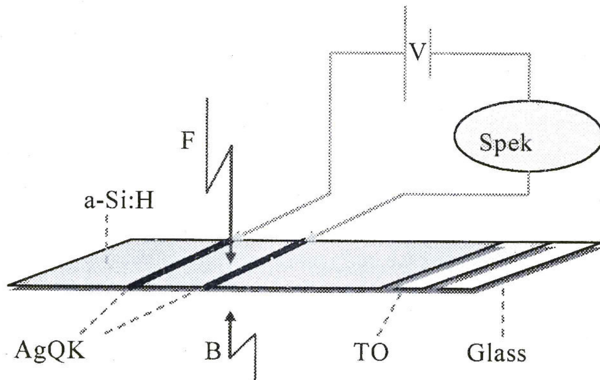

Fig. 4 *Schematic overview of a transversal Photocurrent array and the disposition of the layers involved : a – Si:H and TO (Tin oxide) films.*

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

Photovoltaic response

In Fig. 5, we describe schematically the photovoltaic array employed: The configuration is basically the same as in 3.2.a, with an additional metal film (Met) to contact direct to a-Si:H and no transversal electrodes at all. This last arrangement (longitudinal) uses the fact of generation of internal electric champs on both contact sides of the a-Si:H layer, which produce the photoelectric response.

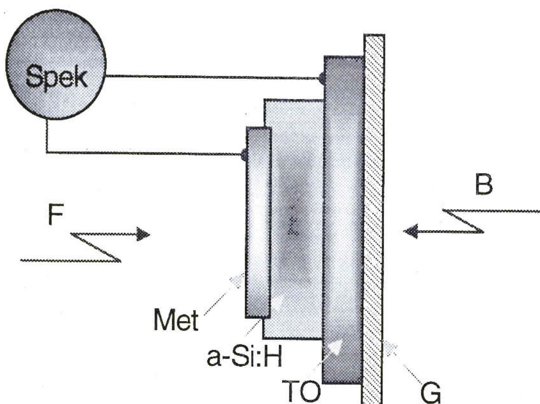

Fig. 5 *Schematic overview of the photovoltaic array and the disposition. of the layers involved in the junctions with a – Si:H.*

RESULTS

In order to explain the procedure applied in this work to interpret the obtained spectra, we restrict the description to one of them, which can be considered the most representative of this series: 13M1

Transversal photocurrent spectrum (13M1)

Fig. 6 shows the result of a transversal photocurrent spectrum, obtained with a a-Si:H layer deposited on a stainless steel substrate, when light incide on it from the frontal side.

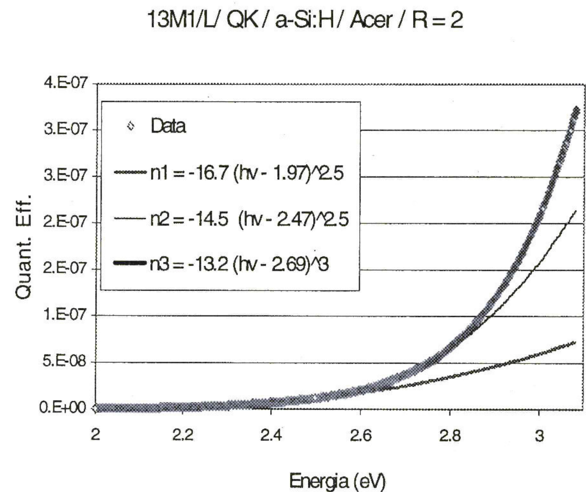

Fig. 6 *Quantum efficiency spectrum of the photoresponse, obtained from a a-Si:H layer deposited on a stainless steel substrate: probe (13M1) in a transversal configuration with frontal illumination.*

From photoresponse spectrum Fig. 6, we can identify, by conventionally deconvolution proceeding [8], three independent contributions to the total response, which can be summarized as:

- $\eta_1 = + [\exp(-16.7)]\ (h\nu - 1.97)^{2.5}$
- $\eta_2 = \eta_1 + [\exp(-14.5)]\ (h\nu - 2.47)^{2.5}$
- $\eta_3 = \eta_1 + \eta_2 + [\exp(-13.2)]\ (h\nu - 2.69)^{3}$

As observed from fig. 6 the theoretical fitting agrees very well with the experimental data. The interpretation of this result is shown in fig. 7, using a energy band model.

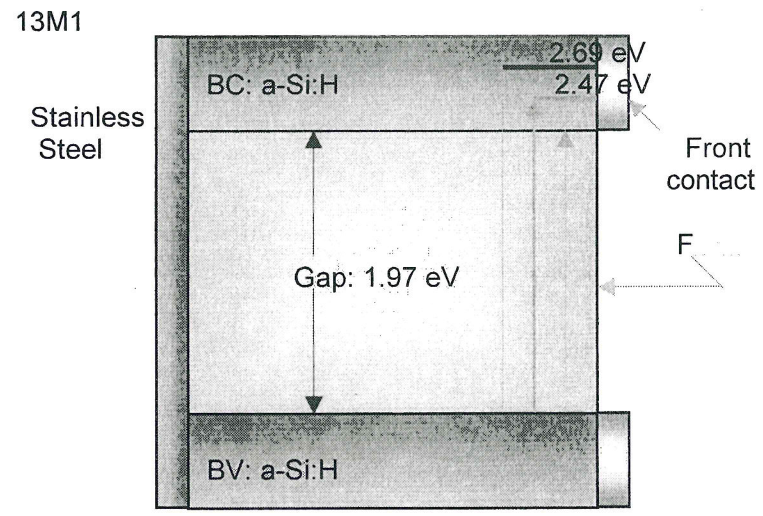

***Fig. 7** Energy band model from probe 13M1, which explains the results from spectrum Fig. 6.*

The observed contributions takes place at the front side of a-Si:H, due first to a band - band transition (1.97 eV) and in second place, two band – localized states transitions (2.47 eV and 2.69 eV), which promote electrons in the conduction band.

From this measurements, we identified the value 1.97 eV as the effective optical band gap of the material (a-Si:H) as will be discussed later.

Summary of photovoltaic transitions: a-Si:H

In this work, we have evaluated nearly 35 photocurrent spectra from a-Si:H and its junctions. Fig. 8, summarizes all photoactive transitions (in eV) detected by us (green marks) and its occurrence grad.

In order to compare our results with known data, Fig. 8, shows also the reference data (gray marks) described in part 2 (Fig. 1), indicating a very good correlation, which will be commented in the discussion section.

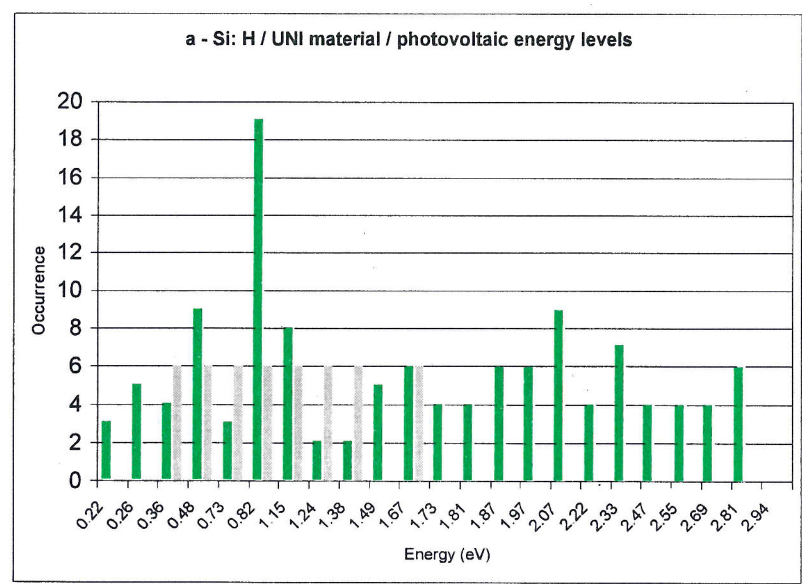

***Fig. 8** Summary of photovoltaic transitions found in this work for a-Si: H and its Junctions (green), the gray marks corresponds to the reference data Fig. 1.*

Fig. 9 resumes the position into the a-Si:H gap of the principal localized levels (Traps) correlated to the, in this work, detected transitions Fig. 8.

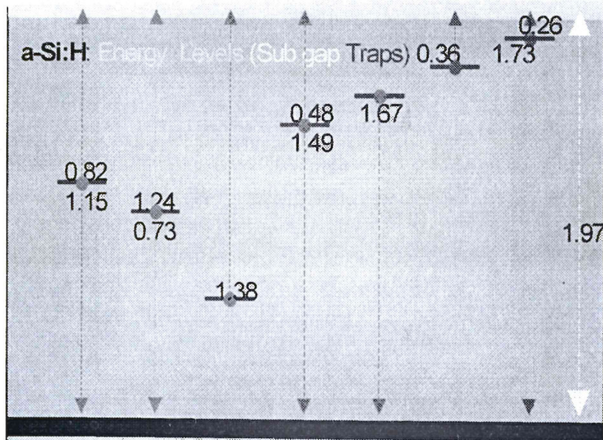

Fig. 9 *Localized energy levels (Trap states) in the band gap of a-Si:H, found in this work (units in eV).*

As a matter of fact, the detection of complementary energy values confirms the determination of the effective optical gap from the material, as was shown in a previous work [10]. In this case, we found the value of 1.97 eV for the gap energy of our a-Si:H.

The complementary values are (in eV): 0.82-1.15, 1.24-0.73, 0.48-1.49, 0.26-1.73.

DISCUSSION

In order to be clear in reference to the results obtained in this work, we must make the annotation, that the done measurements (photocurrent response), were made at the limit of performance of our spectrometer, which in practice means an increment of the error deviation of the energy data up to ± 0.03 eV.

Our present spectral photocurrent results do not only confirm results which have already been obtained (though in a much more elaborate and indirect ways) or expected, but they also reveal other defect states as well as their nature. Indeed due to the untypical procedure followed in this work, in the elaboration of a-Si:H, we expected to find more disorder as normally found in a-Si:H (device quality), corresponding to the occurrence of new (not observed) defect states.

Turning to the determination of the optical band gap of a-Si:H, there is still strong controversy on this subject [2], giving a remarkable discrepancy between the different experimental determined values (reflection, transmission or absorption measurements). In this connection, the most important characterization is the Tauc optical gap (absorption measurements), which bases on the Tauc approximation. Nevertheless, the Tauc optical gap determination can be considered an underestimation of the effective optical gap, due to the fact that this procedure takes account of transitions in between tail bands.

Previous measurements (Photoacustic) done in a-Si:H by our group [19], determined the Tauc optical band gap to be E_{Tauc} = 1.38 eV, unless from transmission measurements one could estimate the optical gap to be nearly E_g = 2.00 eV.

In reference to the analyzed a-Si:H probes, we must remark the diversity of cases evaluated (Thermal treated, non treated, different metal junctions), The purpose of using different types of samples was to test the universality of our conclusions as well as to test the individually influence of each step. This conclusions will be reported later (Tesis de Licenciatura).

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Recepción de originales: Setiembre 2005
Aceptación de originales: Diciembre 2005