

# New Principles in Design and Technology of Multi-junction Solar Energy Converters

Chávez-Urbiola Iker, Vorobiev Yuri, and Ramirez-Bon Rafael

**Abstract**—The multi-junction solar energy converters can be made cheap and efficient, if some new principles are applied for their design. We propose to make each p-n junction of the converter electrically independent with its own contacts. It eliminates obligatory series connection of the junctions, and allows using wide variety of electrical schemes, of “p” and “n” layers sequence, as well as of materials used. In particular, cheaper II-VI semiconductors can be used instead of III-V ones, with essentially simpler and cheaper technologies, such as Chemical Bath Deposition (CBD), Chemical Vapor Deposition (CVD) and their combination. Several structures were created to illustrate the principles stated, and the results of their characterization are presented.

**Index Terms**—Multi-junction solar cells, variable electrical connections, II-VI semiconductors, two-stage CBD-CVD technique, photo-chemical bath deposition.

## I. INTRODUCTION

It is well known that relatively low efficiency of conventional solar cells (around 15%) is a consequence of a wide solar spectrum, so that several semiconductors with different band gaps are necessary to utilize the major part of the spectrum. This is realized in multi-layers (multi junction, or tandem) solar energy converters, see [1]-[4], that have efficiency of 30–40%, with a recent record of 44.7% [4]. It must be noted that tandem construction is a widely accepted way of design of different efficient solar energy converters, like thin film Si-based cells [5] or polymer ones [6].

In tandem devices, the individual p-n junctions are connected in series; therefore the less efficient junction determines the total photocurrent. To eliminate this drawback, we suggested [7], [8] that individual junctions can be separated electrically, which immediately gives additional degrees of freedom in device design, in optimization of the connections, including the different sequence of “p” and “n” layers, which can be prepared from the larger variety of materials. Finally, it gives a possibility to construct efficient and economic solar energy converters. In particular, instead of III-V materials and MBE technology normally used for production of tandem devices, the cheaper II-VI materials with simpler and less energy consuming CBD-CVD (Chemical Bath Deposition — Chemical Vapor Deposition) technologies can be used for construction of converters in accordance with our suggestions. Here we describe the new

system design, and give an example of application of the techniques mentioned, together with some preliminary results.

## II. DESIGN OF MULTI-JUNCTION CONVERTERS WITH VARIABLE SEQUENCE OF P-N LAYERS

We suggest that each semiconductor p-n junction in the converter has electric contacts at both ends, and in case of 2-junction device, an insulating layer is introduced between the two materials (Fig. 1 left — scheme of energy bands; Fig. 2 — device construction). No tunnel junction exists here. These two separated electrically cells can be connected in series, like it is in traditional tandem. However, if several converters of this kind are working, there are other possibilities of parallel/series connection, so that voltage and current of the whole battery will be optimized (see [7] for some examples).

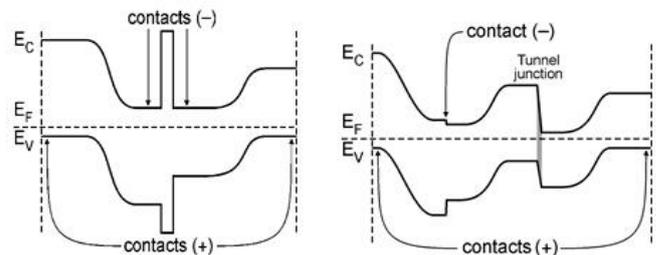


Fig. 1. Energy band diagrams of multi-junction converters with 2 (left) and 3 (right) semiconductor p-n-junctions.

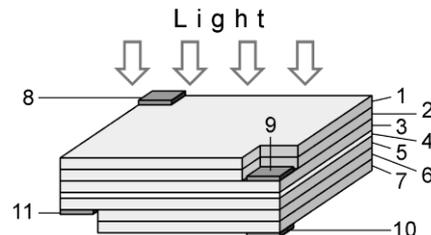


Fig. 2. Possible construction of a 2-junction converter. 1: p-layer of cell 1; 2: i-layer of it; 3: n-layer; 4: insulating layer; 5: n-part of cell 2; 6: i-part; 7: p-layer of cell 2; 8-11: contacts.

In 3-junction device, there is a possibility to avoid the insulating layer (Fig. 1 right), with only one tunnel junction instead of 2 in traditional tandem. In this last case, the cell made of material with the largest band gap should be connected in parallel with tandem of the two other cells with smaller gap, providing that this tandem produce approximately the same voltage as the first cell. This separation of junctions allows much larger variety of materials to be used, thus giving a possibility to reduce the device cost.

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Besides the materials' cost, that of technology is essential for the total cost estimation. Many of II-VI compounds can be elaborated with CBD and CVD techniques that do not demand complicated equipment and can be realized at relatively low temperatures, with small energy consumption.

Below we describe the experimental procedures and some preliminary results. Our goal was a converter made of 3 semiconductor materials, for example, with central layer of Si, and the two adjacent of PbTe and CdTe (CdSe), with the sequence of gaps as approximately 1.5 (1.7) eV, 1.1 eV and 0.4 eV, that looks appropriate to cover all the solar spectrum. Now we present the results for Si — PbTe diode that makes an essential part of the whole device.

### III. TECHNIQUES OF FORMATION OF SEMICONDUCTOR LAYERS

Previously [9] we reported a CdS/PbS solar cell made as a whole by CBD technique, with quantum efficiency of 25%. In the present work, we combine two cheap low temperature deposition techniques: chemical bath deposition (CBD), which easily provides good adherence to the substrate, with chemical vapor deposition (CVD), which normally gives a large grain size and therefore high lifetime of charge carriers, usually with a high deposition rate. Based on this scheme, we reported the setup of a CVD system with a single chalcogen source to obtain cadmium or lead chalcogenides by conversion of cadmium or lead oxides/hydroxides previously deposited by CBD. Conversion to chalcogenide films is attained by thermal ion exchange exposing the precursor metal oxide film to the chalcogen gas flux at high temperature (for the details, see [10]). We applied it to the deposition of PbTe films from a lead based compound plumbonacrite ( $\text{Pb}_{10}(\text{CO}_3)_6\text{O}(\text{OH})_6$ ) deposited at first stage by CBD under UV illumination (actually, it is Photo Chemical Bath Deposition, or PCBD). At the second stage, Te hot gas was used as the chalcogen source in CVD reactor. In a similar way, CdSe films were obtained by conversion of CBD\_made substrates of cadmium oxide/hydroxide, with a Se chalcogen source [11]. Using the *n*-Si substrate covered with plumbonacrite by CBD, in a CVD reactor with Te source we obtained *n*-Si-*p*-PbTe structures, with PbTe layer thickness of around 1  $\mu\text{m}$ .

The plumbonacrite film was made in a solution prepared in a 160 ml flat beaker by the sequential addition of 0.2M of  $(\text{CH}_3\text{COO})_2\text{Pb}\cdot 3\text{H}_2\text{O}$ , (40 ml of lead acetate, trihydrate), 0.4M of  $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7\cdot 2\text{H}_2\text{O}$  (40ml of sodium citrate, dihydrate), 0.5M of KOH (potassium hydroxide). The solution was added with deionized water to complete a total volume of 160 ml. Then the solution was placed under UV radiation with a UV lamp (364 nm main web radiation, 22 W, see Fig. 4) at room temperature to realize a PCBD process; a white dense thin film can be seen after 5 hours. Without illumination, the deposition time necessary is almost 20 times larger. The dissociation of lead acetate gives the metal ions with the action of the complexing agent, also provides the basis for the formation of ions  $\text{CO}_3^{2-}$ , as well as the KOH provides  $\text{OH}^-$ ,  $\text{O}^{2-}$  and  $\text{K}^+$  ions which are employed in the main formation reaction. The formulation used in this work is easier to

prepare than one described in [12], due to the smaller amount of components; the actual process is faster due to the use of UV light.

The plumbonacrite film was placed in quartz chamber above of Knudsen pipe with tellurium powder (99.9% purity) in a nitrogen atmosphere at 500 °C, all this is sustained by a defined time until plumbonacrite transforms to PbTe.

The PCBD technique was described earlier [13], [14], and used for deposition of semiconductors like CdS and ZnS. In these previous papers, the deposition process was not possible without UV illumination; in our case, the deposition without illumination is possible, but with much slower rate. We believe that UV light acts as important factor in liberation of ions necessary for the deposition reaction, thus greatly accelerating it. The similar effect of UV radiation was observed in chemical bath deposition of some other semiconductors, PbS for example.

### IV. RESULTS AND DISCUSSION

The X-ray diffraction measurements (Fig. 3) confirmed that PbTe layers were formed on Si substrates, with complete conversion of plumbonacrite to lead telluride during 40 min of exposure to Te gas flow, the necessary time to transform the precursor material depends on the film thickness (for higher thickness it requires a higher time under the tellurium hot gas).

The PbTe film shows an average crystal size of 29 nm (found using the program WinJade with constant FWHM). Lattice constant "*a*" was calculated according to Bragg's Law, interplanar spacing equation and using the principal plane (200), we obtain  $a = \lambda / \sin \theta$ , where  $\lambda$  is the wavelength of the X-ray beam ( $\text{Cu}$ ,  $\lambda = 1.54056 \times 10^{-10} \text{m}$ ) and  $\theta$  is the diffraction angle ( $2\theta = 27.64^\circ$  for (200)). Lattice parameter "*a*" = 6.44 Å that is in concordance with its power diffraction file (PDF 38-1435 "*a*" = 6.45 Å); The labels in each peak correspond to the crystalline planes (*h*, *k*, *l*). The silicon planes do not appear due to the large thickness of the film.

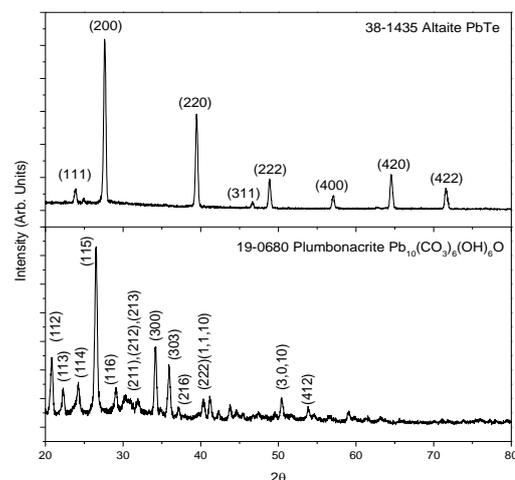


Fig. 3. X-ray diffraction pattern of lead telluride film and plumbonacrite film.

The optical properties of PbTe films were studied by diffuse reflection measurements, using the Kubelka-Munk procedure to find absorption coefficient. The derivative of the

absorption spectrum obtained is presented in Fig. 5. Peak at 0.31 - 0.35 eV corresponds to the material's absorption edge.

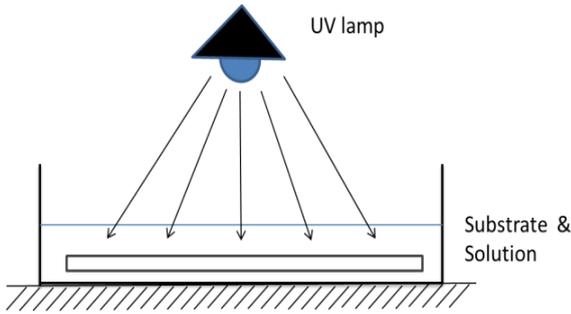


Fig. 4. Photochemical bath deposition scheme.

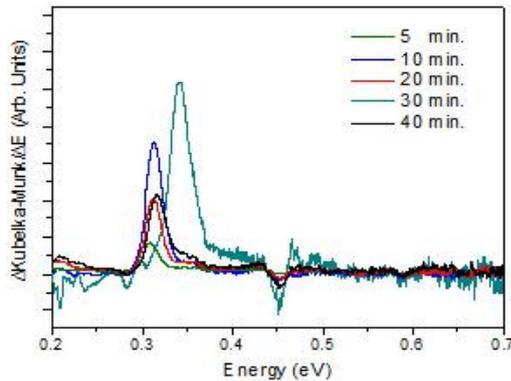


Fig. 5. Derivative of the spectra of absorption coefficient of PbTe layers.

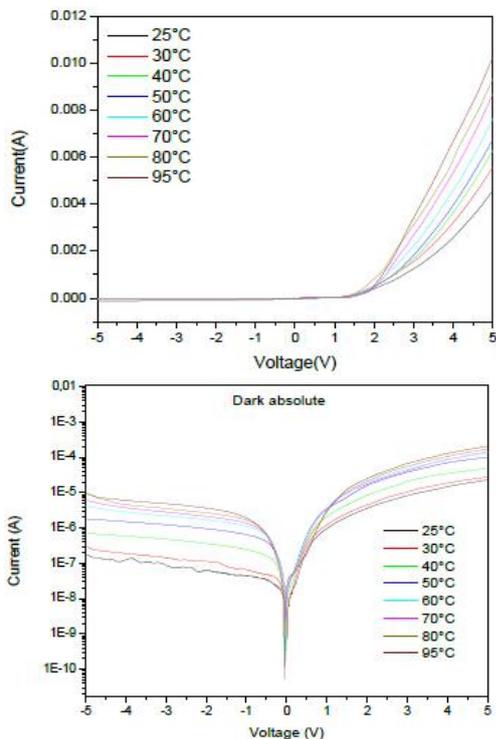


Fig. 6. Current-voltage characteristics of the diode CVD- made during 40 min (details in the text).

Fig. 6 shows the current-voltage characteristics of *n-Si-p-PbTe* diode obtained, at different temperatures (upper part in lineal scale, lower in logarithmic one). It is seen that both branches grow with an increase of temperature; the variation of reverse current follows exponential law, in agreement with theory. The activation energy of this dependence is 0.33 eV, so it exactly corresponds to PbTe

band gap.

The I-V characteristics have clearly rectifying character, with ratio of direct to reverse current at 5V around 300 at 25°C, decreasing to 50 at 95°C. Thus, the structure made has quite satisfactory diode parameters. The lower part of Fig. 6 presents detailed information about direct and reverse parts of diode's characteristics.

The Fig. 7 shows that illumination of the diode produces photocurrent, so that structure is really acting as solar cell, with a poor fill factor (around 20%) leaving large space for device perfection. Device scheme is given inside the figure. Black line corresponds to the darkness, and the red one to the cell illuminated by Solar Simulator (room temperature). The parameters are given at the table nearby; it could be seen that the cell efficiency is 0.074 %.

Using similar CBD-CVD technique, we succeeded in production of many other useful for solar applications semiconductors, such as CdSe, CdTe, PbS, PbSe (see [10] for some details). The design of multi junction solar cells using these materials is our next goal.

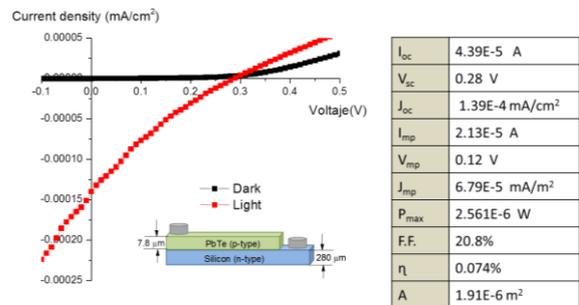


Fig. 7. I-V characteristics of Si-PbTe diode, and its parameters. The black line is obtained in the darkness, red one — with illumination.

## V. SUMMARY

We claim that in construction of multi junction solar energy converters, the choice of materials and technologies can be greatly enlarged, if the individual semiconductor diodes are electrically separated, each one having own contacts. In this case, the converters' parts made of materials with different band gaps can be connected in optimal way, to gain maximum current and voltage. The use of II-VI materials, like CdS, CdSe, CdTe, PbTe as well as CBD-CVD technologies can essentially reduce the device cost, preserving high conversion efficiency. The first experiments performed prove the feasibility of this approach and its great potential in devices' improvements.

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