QUANTUM CONFINEMENT EFFECTS IN A GLASS/ITO/CDS/CDTE SUPERSTRATE STRUCTURE DESIGNED FOR SOLAR ENERGY CONVERSION

[1]Y.V. VOROBIEV, [2]I.R. CHÁVEZ-URBIOLA, [3]S.A. PÉREZ-GARCÍA, [4]P. VOROBIEV

[1,2]CINVESTAV-Querétaro, Libramiento Norponiente #2000, Querétaro 76230, QRO, México.
[3,4]CIMAV/Monterrey, Alianza Norte 202, PIIT, Monterrey 66628, N.L., México.
E-mail: [1]vorobiev@cinvestav.mx, [2]pavel.vorobiev@cimav.edu.mx

Abstract- Investigation by XPS of the composition along the CdS/CdTe bilayer which is the active part of a CdTe-based solar cell, substantiated by Kelvin Probe work functions measurements, revealed existence of quantum wells near boundaries of both parts of the bilayer that affect the performance of solar cell. Photoluminescence measurements confirm the existence of quantum wells and of the corresponding blue shift of electron transition energies. Analysis of energy band diagram of the structure shows that the bilayer is of n^+-n character (i.e. without p-n junction) and has several potential barriers that are responsible for the photo voltage generated by illumination. Traditional treatment with $CdCl_2$ enhances the barrier at n^+-n interface and improves the cell's characteristics.

Keywords- Quantum Confinement, Solar Cell, CdS/CdTe Active Layer, Band Diagram.

I. INTRODUCTION

CdTe-based solar energy converters occupy a solid position in the market of renewable energy devices (it is the second most abundant photovoltaic technology in the world marketplace after crystalline silicon, representing in 2014 7% of the world market, for more details see [1-3]).

The common CdTe solar cells consist of a simple heterojunction structure containing a p-doped CdTe light absorbing layer matched with an n-doped CdS film, which acts as a window layer. The illumination takes place through glass superstrate covered with Transparent Conductive oxide TCO (like ITO) layer, CdS film deposited over the TCO. Typical CdTe thin-film deposition technique employed is a close-spaced sublimation, from earlier patents up to the latest technological solutions [4, 5].

This technique is simple, quick, cheap and efficient; however, it does not allow precise control of the deposition parameters, and thus of the characteristics of the resulting structure.

To investigate an effect of the deposition parameters upon the characteristics of cell's components, we have chosen slower and much more controllable technology of CdTe film production, namely, a Chemical Vapor Deposition (CVD) in Hot Wall CVD reactor, with separate Cd and Te atomic sources and transportation of the corresponding vapors with neutral gas flow, leaving the deposition of the CdS window layer by usual CBD method (Chemical Bath Deposition) [4, 5]. This paper presents the results of experimental investigation of the developed Glass/ITO/CdS/CdTe superstrate solar cell structure and its components, in particular, effects of the near-surface quantum wells upon the cell's performance.

II. MATERIALS AND METHODS

Structures for investigation were of the same type as industrial CdTe-based solar cells: Glass/TCO/CdS/CdTe/Graphite electrode. To be able to control parameters of the different layers, we had also made samples of CdS and CdTe films on glass substrates with the same thickness as that used for light converting structures. As TCO (Transparent Conductive Oxide) the commercial ITO film/on glass was used. The formulations and processes to obtain CdS film by ammonia-free CBD were the same as those described in [5].

Deposition of CdTe in Hot Wall CVD reactor corresponded to that described in [4] with temperatures of both Cd and Te sources varied between 450 and 600 $^\circ$C, substrate temperature at all cases was by 50 $^\circ$C less than sources temperature. The argon transporting gas flow of 1.5 lt/min was employed. The evaporation rate of Cd and Te from the sources made as Knudsen cells was controlled by the size of the opening in the cell; both sources produced practically equal gas flow. Cd and Te melting temperatures are around 321 $^\circ$C and 449 $^\circ$C correspondingly; for this reason, the saturation vapor pressure of Cd, for example, at 600 $^\circ$C is approximately two orders of magnitude higher than that of Te. Thus we manipulated with Knudsen cells opening diameters to equalize Cd and Te vapor fluxes.

The deposited CdTe thin films were characterized by X-ray Photoelectron Spectroscopy (XPS), X-ray diffraction (XRD), Kelvin Probe measurements, scanning electron microscopy (SEM) and UV-VIS diffuse reflectance spectroscopy. The current versus voltage (I-V) characteristics of the ITO/CdS/CdTe heterostructure in the darkness and under 100 mW/cm^2 illumination were measured using a Semiconductor Parameter Analyzer 4155C Agilent.

III. RESULTS AND DISCUSSION

XRD patterns for CdTe films at different temperatures showed a polycrystalline nature for all films, which is consistent with the standard cubical structure of cadmium telluride (Powder Diffraction File PDF 17-0750). In Fig. 1 the top views are shown of the CdTe films grown at different sources temperatures: (a) 450 $^{\circ}$C, b) 500 $^{\circ}$C, c) 550 $^{\circ}$C, d) 600 $^{\circ}$C). Here a dense film is observed composed of geometric grains. The grain size increases as increases the temperature, the size increment goes as 0.37μm, 1.67 μm, 3.02 μm and 6.4 μm for temperatures mentioned above. For a solar cell structure, the films with largest grains were used, and all the subsequent results refer to these films.
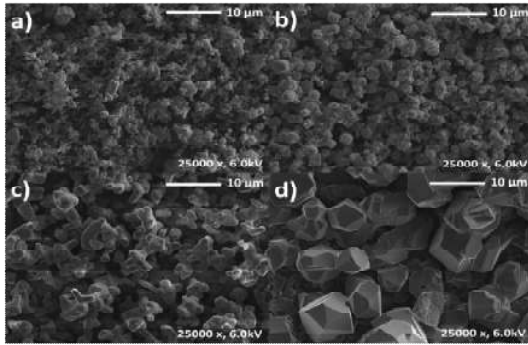

Fig. 1. SEM images of CdTe films grown at different source temperatures

Fig. 2 presents the XPS data for CdS/ITO cell component giving a distribution of elements along the sample. The abscissa shows the etching time (180 s with etching rate of 0.66 nm/s gives the CdS film thickness of 120 nm, etching rate was calibrated with Ta_2O_5 standard). Here we observe a deficit of S atoms compared to Cd, giving the n-type conductivity (sulfur vacancies acting as donors, like F-centers in alkali halides). Besides, sharp increase of oxygen content at the CdS/ITO interface is seen.
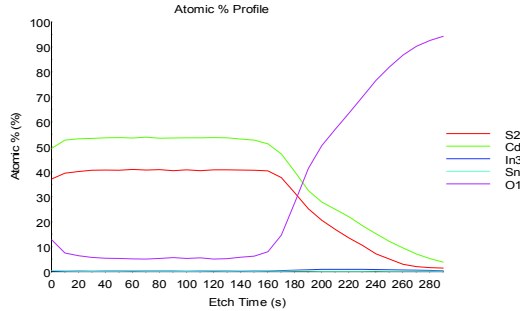

Fig. 2. Distribution of elements in sample CdS/ITO on glass.

The effect of oxygen is confirmed by variation of sulfur binding energy (Fig. 3). According to NIST data [6], this energy for S 2p line is 162 eV, which approximately corresponds to the line position in the outer part of the film. In the part adjacent to ITO, the binding energy shifts to 165 eV thus showing an effect of oxidation. Most probably, oxygen diffuses

from ITO during the deposition process. For CdTe film XPS shows close to stoichiometric elements distribution (Fig. 4) with large non-stoichiometry in thin near-surface layer. From the variation of the Te 3d signal binding energies (Fig. 5 for Te 3d level; for Cd we have similar data) the oxidation effects are evident (the presence of oxygen) at near-surface region: binding energies for the Te 3d signal of the Te $3d^{5/2}$ 575 eV and Te $3d^{3/2}$ 585 eV at the outmost part of the cell, and shifting to Te $3d^{5/2}$ 572 eV and Te $3d^{3/2}$ - 582 eV deeper in the cell. According to NIST database [7], internal values are those characteristic for the bulk CdTe, external are shifted to higher energies due to oxidation.
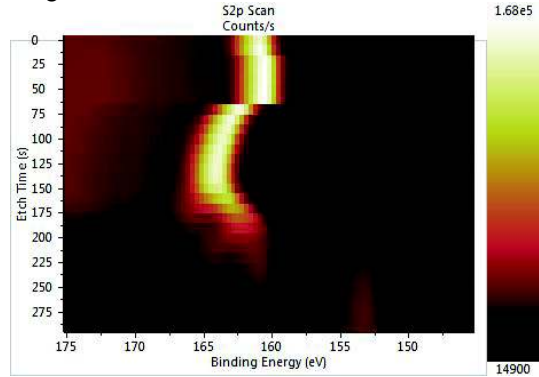

Fig. 3. Binding energy of S atoms

It is known that an excess of Cd present near the CdTe film surface (vacancies of Te) produces donors in CdTe, and the Oxygen (isovalent impurity) also acts as a donor. Thus we came to the conclusion that at least the near-surface part of CdTe film in our CdS/CdTe system is definitely of n-type that will be reflected in the band diagram below. Measuring the sample work function with Kelvin Probe equipment, we found that all CdTe film has n-type conductivity.
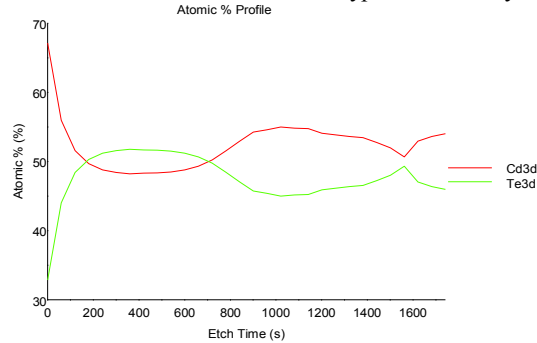

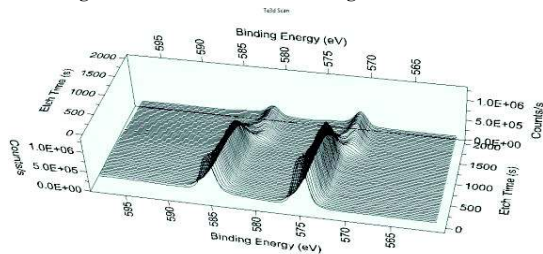**Fig. 4. Elements distribution along the CdTe film.**

Fig. 5. XPS binding energies for Te 3d level in CdTe.

We see that both semiconductor films in the bilayer studied have thin (of order of 10 nm) near-interface layer with a composition different from that of the bulk. Photoluminescence (PL) measurements showing the blue shift of electronic transitions from the band gap energy suggest that these layers can be treated as quantum wells with the corresponding quantum confinement effects.
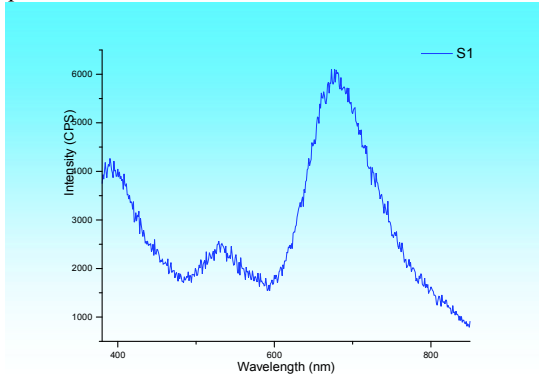

Fig. 6. Photoluminescence (PL) spectrum of CdS film

In PL spectrum of CdS (Fig. 6) we see the bands at 400, 530 and 680 nm corresponding to photon energies of 3.1, 2.34 and 1.83 eV. The last two are related to the defects, and according to [8] can be ascribed to S interstitial atoms (2.34 eV) and Icd – Vcd complexes (1.83 eV). But the first band exceeds the bulk band gap value by approximately 0.6 eV and definitely indicates the quantum confinement effect. In PL spectrum of CdTe film (not shown) we observed a broad peak between 1.7 and 2 eV, also greatly exceeding the bulk band gap value. Fig. 7 shows the PL spectrum of the CdS/CdTe bilayer; here again we see the band at around 420 nm (3 eV) of the CdS film, and at 750 nm (1.66 eV) of CdTe.

For estimation of possible quantum effects in semiconductor nano layers, we shall use formulas obtained in our previous papers [9, 10] for quantum wells and dots of different shapes. According to the XPS data above, there are sharp variations of charge carrier concentrations at CdS and CdTe regions adjacent to interface and surface, following the variations in the stoichiometry observed.
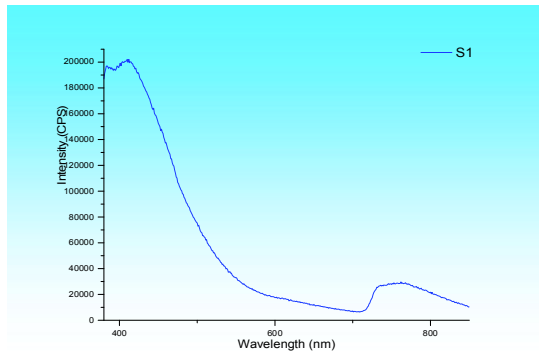
The change in charge carrier concentration affects the refractive index of the material, and variation of the refractive index causes light reflection at the boundaries of the corresponding regions. It allows us to treat these near-boundary regions as quantum wells formed by the mirror reflective planes, and apply for their description the so-called Mirror Boundary Conditions developed in our publications [9, 10]. The expression describing electron transition in one-dimensional quantum well (i.e. thin semiconductor layer of thickness a) will be

$$E = h\nu = E_g + h^2/(8\square a^2)$$

where E_g is the bulk band gap, h is Planck constant and $\square$ is exciton reduced mass (equal to 0.134 m_o in CdS and 0.094 m_o in CdTe, m_o being the mass of free electron). To explain the observed blue shift in CdS, the well thickness a ought to be 5 nm, and in CdTe – 10 nm, which is of the correct order of magnitude (see Fig. 2 and 4).

Thus we came to the band diagram of our solar cell structure (Fig. 8). Here we show an increase of CdS band gap near interface with ITO (that includes up-bending of c-band near ITO layer due to the difference in materials work functions) and an increase of CdTe band gap near its boundary with CdS, both due to quantum confinement effects. The potential barrier in c-band at CdS/CdTe boundary of around 0.4 eV defines the open circuit voltage generated under illumination (it increases to 0.6 eV after standard CdCl$_2$ treatment, these results will be published separately). A small up-bending of CdTe valence and conduction bands at its interface with graphite defines the photo voltage of 0.2 V generated at illumination of the structure from CdTe side, detected during measurements of the contact potential of CdS/CdTe bilayer with the Kelvin Probe method. We note that the absence of a p-n junction even in efficient CdS/CdTe solar cells was already mentioned in publication [11].
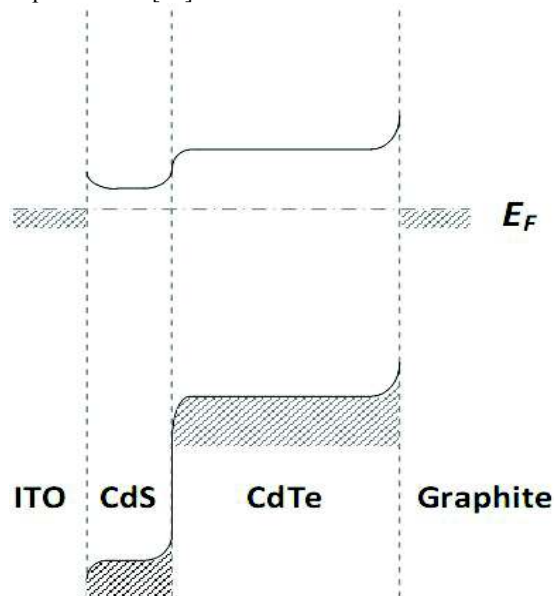

Fig. 8. Energy band diagram of the solar cell structure.

Fig. 7. PL spectrum of CdS/CdTe bilayer

The quantum confinement effects observed, in general, are useful for the solar cell performance since an increase of the CdS band gap improves its action as a window layer, and similar effect in CdTe widens its sensitivity spectral region. On the other hand, the variation of the CdS band gap near its interface with ITO brings additional series resistance that is a consequence of the high work function of ITO, and has negative effect on the cell parameters.

CONCLUSIONS

We observe the quantum confinement effects in CdS/CdTe active bilayer of a CdTe-based solar cells caused by variation of films composition near their boundaries.

These effects have positive influence upon cell performance. Another conclusion is that the standard construction of CdS/CdTe superstrate cell is not ideal for solar energy conversion, giving the incorrect conductivity type of the main absorber material (CdTe film), and having additional serial resistivity at the ITO/CdS contact. Therefore, we plan to investigate and develop a different construction of efficient solar energy converter.

ACKNOWLEDGMENTS

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