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Preparation of Nanosized CZTS Structures for Solar Cells

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Abstract – **In this work, we report some preliminary results concerning the fabrication of quaternary semiconductor Cu_2ZnSnS_4 (CZTS) thin films on a flexible substrate through the simultaneous electrodeposition of elements having different standard electrochemical potentials. CZTS thin films were obtained by potentiostatic deposition from aqueous baths at room temperatureand under N_2 atmosphere, varying bath composition. Chemical composition and structure of the electrodeposited films were evaluated by EDS, SEM and XRD. Preliminary results on the photoelectrochemical behaviour of the films will be also presented. We obtain CdTe thin films with good physical properties, these samples can be used as window material in CdTe/CZTS solar cells to improve the photovoltaic efficiency.**

Keywords – **Cu_2ZnSnS_4, CZTS, CdTe, Thin Films, Solar Cells, Electrode Position.**

I. Introduction

Solar cells based on semiconductor thin films are emerging as alternative to silicon; however, the materialsgiving the highest efficiency, CdTe and CuInGaSe, contain toxic (Cd) and rare and expensive (In and Ga) elements. In this field, the challenge is to substitute In, Ga and Cd with abundant and non-toxic elements without lowering the high efficiency achieved with these technologies. In this way, it could be possible to avoid the possible shortage in the supply of these elements, which would inhibit a cost-effective large-scale production. Alternative compounds which contain more abundant and less toxic elements, based on copper, zinc, tin and sulfur (CZTS), are potentially promising materials, because they present all the above listed features. CZTS materials are characterized by a direct band gap of about 1.5 eV and by a high absorption coefficients of visible light (up to about 104 cm-1) [1].

The actual deposition methods applied in the fabrication of CZTS thin films (thermal evaporation, atom beam sputtering, hybrid sputtering, photochemical deposition, pulsed laser deposition, screen printing, electron beam evaporation) require complicated equipment and are very expensive. In this field the electrochemical route appears of great interest because easy to conduct, it is a non-vacuum and low-cost technology, working at room temperature and using non-toxic solvents and reagents, with high throughput and high materials utilization. Moreover, electrodeposition has the advantage of being an industrially established process for large area semiconductor deposition with superior uniformity in composition. In fact, up to date, the literature shows that non-uniformity in composition and/or the presence of secondary phases prevent the obtainment of electrochemical CZTS thin film of high quality [2-3].

In the present work, the aim is to optimize the electrochemical deposition process on flexible substrate in order to obtain a high quality CZTS thin film. On the basis of the knowledge acquired by our research group on the production of CIGS thin films and nanowires through electrochemical route, we report some preliminary results concerning the study on the fabrication of CZTS thin films obtained by one-step potentiostatic deposition from aqueous bath.

CdTe thin films as window material is the most used in thin film photovoltaic solar cells technology (CdS, $Cu(In,Ga)Se_2$, Cu_2ZnSnS_4) [4-7]. The thin films solar cells technology requires deposition methods to ensure simplicity, low production cost and high efficiencies. Chemical bath deposition has proven to be one of these methods. The efficiency is influenced by the transport of charge in the hetero-junction between both, the window and absorbers materials when solar cells are fabricated. Chemical bath deposition (CBD) technique is well suited for producing large area thin films for solar energy applications, and the number of possible materials to be produced through this technique is bound to multiply in subsequent years; this is due to the feasibility to produce multilayer films. CBD has demonstrated to be a simple and low cost technique to prepare CdS films as optical window for solar cells. [8-11].

Many options are required to improve CBD for technological applications. Other authors use an additional illumination by halogen lamp during the growth of films; all in order to improve the physical properties of CdTe thin films. In aim this work is to study the impact on the main physical properties of the CdTe thin films deposited by chemical bath deposition technique (CBD) using substrates with different thermal treatments and under different growth conditions with the porpoise to obtain adequate CdS thin films to be used in large areassolar cells technology [12-13].

II. Experimental

CdTe semiconductor thin films were deposited on SnO_2: F substrates (TCO) by CBD and photoassisted-CBD (P-CBD) technique, for the last we used a halogen lamp with a density power of $100mW/cm^2$. As precursor solution we used $CdCl_2$ (0.1M), NH_4Cl (0.2 M), NH3 (2 M) and TeO_2 (0.3 M). Some substrates were treated with HCl (0.1M) during 30 min, and others were annealed at 500°C in different atmospheres (Ar, O_2 and air). Bilayers of CdTe with deposition time of 10 min. at 75± 2 °C were obtained.

CZTS thin films were electrodeposited potentiostatically on ITO substrates supported by polyethylene terephthalate (PET). Before deposition, a substrate pre-treatment consisting in an ultrasonic degreasing in organic solvents (first step: acetone, second step: isopropilic alcohol, 15 min each step) was adopted [10], in order to obtain uniform deposits. Depositions were carried out potentiostatically under nitrogen atmosphere at room temperature from a de-aerated aqueous solution containing CuCl (0.02M), $ZnCl_2$ (0.02M), $SnCl_2$ (0.04M) and $Na_2S_2O_3$ (0.4M). To optimize the stoichiometry of the deposit, electrochemical baths with different compositions, obtained mixing different volumes of the above-mentioned solutions, were tested. The final pH was about 5, it was obtained adding lactic acid and NaOH (15M). Electrodeposition was performed for 45 min, at a potential of -1.05V vs. saturated calomel electrode (SCE); electrochemical experiments were performed using a PAR potentiostat/galvanostat.

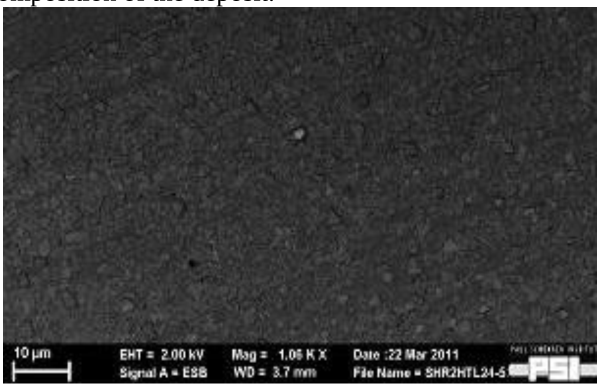
The structural characteristics of the samples were determined by the X-ray diffraction patterns (XRD), by means of a D-500 Siemens X-ray system using the CuKα line. (λ= 0.154nm) as the source, with a step of 0.02° and a measuring time of 0.5s for each step. The layer thicknesses were measured with a step profiler (Sloan Dektak II). Morphological analysis was made using a scanning electron microscope (SEM) JEOL JSM-6300 model with a voltage of 5 kV, allowing a resolution of 2nm, and an AFM, using contact mode with phosphorus tipped (n) doped with Si. A standard three-electrodes cell was employed, with a platinum net as counter electrode and a SCE as reference. Optical properties were obtained using a Shimadzu UV 2401-PC spectrometer. The CdTe thin films were also thermally treated with $CdCl_2$; we used as back contact, two evaporated layers of Cu and Ag (20 Å and 350nm, respectively) with an area of 0.08 cm^2 onto the CdTe later annealed at 180 °C in Ar.

In order to ensure the reliability of the different characterizations, these were performed on different pieces of the same sample. Chemical composition of CZTS thin films was evaluated by energy-dispersive spectroscopy (EDS). Photoelectrochemical behaviour of the as-deposited thin films was investigated at room temperature in an aerated 0.1M Na_2SO_4 solution using a three electrodes-cell, with a platinum net as counter electrode and a standard mercury sulphate electrode (MSE) as reference. The cell was equipped with flat quartz windows for allowing sample illumination, obtained using a 150W Xe lamp (Oriel) coupled to a UV/visible monochromator, mounted in an optical line with quartz optics. Photocurrent was detected by a two-phase lock-in, connected to a mechanical chopper (frequency: 10 -20 Hz). To suppress second harmonic responses, a yellow filter was inserted in the light path before recording photocurrent at long wavelengths. CZTS/CdTe solar cell were completed using CdTe thin films (thickness of 4 μm).

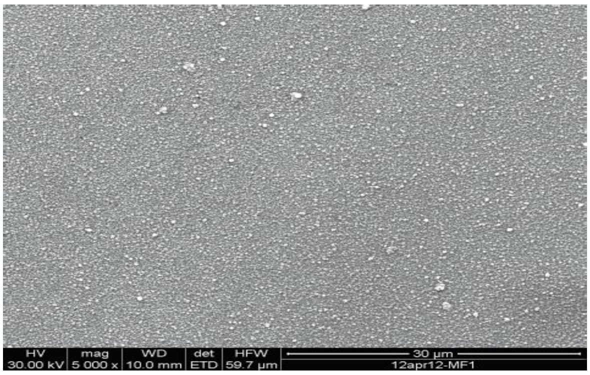
III. RESULTS AND DISCUSSION

Depending on composition of electrolytic bath used for the deposition process, it was possible to obtain different CZTS deposits, characterized by different chemical compositions. It was necessary to investigate different baths prior to find the best experimental conditions leading to CZTS films with suitable composition for solar cell applications. We have checked the influence of bath composition on the kinetics of deposition and on film morphology and composition, varying the volumes of mixed initial solutions.

A compact enough CZTS layer covering uniformly all substrate area exposed to the solution was obtained. The as-deposited thin film was amorphous as revealed by X-ray diffraction pattern, that has not been reported here because practically flat. Thermal treatment would vary the structure of the film, but we didn't perform it because of ITO/PET substrate, which could not be exposed at high temperatures (PET decomposes at about 340°C). In fact, annealing would be efficient at temperatures higher than 400°C and, thus, it is necessary to change the substrate. Further investigations are in progress on other substrates in order to evidence a possible influence of thermal treatment on both crystallographic structure and chemical composition of the deposit.



(a)



(b)

Fig.1. FEG-ESEM micrographs of the as-deposited CdTe and CZTS thin film

The composition of the as-deposited sample was evaluated by a quantitative EDS analysis. Fig. 2 shows a typical XRD spectrum revealing the presence of peaks arising from substrate in addition to peaks of Cu, Zn, Sn and S, due to the deposited CdTe and CZTS thin film.

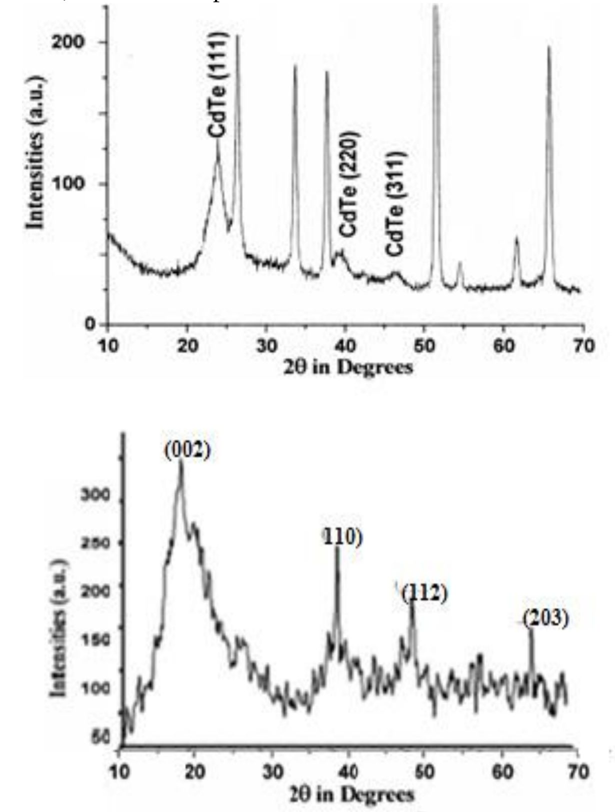


Fig.2. XRD spectrum of the electrodeposited CdTe and CZTS thin film;

The film prepared without complexing agent showed well-covered surface morphology on the substrate with some cracks on the surface of the film whereas those prepared using complexing agent, exhibited uneven and slightly porous and some overgrown particles on the surface of the films. After annealing, morphology changes into the flat grains, uniformly distributed over the entire surface of the substrate.

CZTS thin films were formed after annealing the precursor in a sulphur atmosphere at 500˚C. The doping density of the films was in the order of 10^{16} cm^{-3}. Further investigation of the photovoltaic performance of the corresponding thin film solar cells indicated that the device performed better under low illumination intensity. At high illumination intensity (equivalent to 1 sun), the recombination in the space charge region was increased, leading to the decrease of the performance

The photoelectrochemical behaviour of CZTS thin films was investigated in an aerated 0.1M $Na_2S_2O_3$ solution (pH =6). First the photocurrent response was measured at its open circuit potential (Uoc) and the photocurrent spectrum was recorded. Then, because all films showed cathodic photocurrent, a slight cathodic polarization (-0.1 V vs. Uoc) was applied and the spectrum was recorded.

An optical gap of about 2 eV was estimated from the photocurrent onset wavelength. The measured gap is higher than CZTS crystalline band gap, but considering the amorphous nature of these films it was an expected result, thermal treatment would reduce this value.

CZTS films posess promising characteristics optical properties and aband gap energy of about 1.45 eV to 1.5 eV [14]. As a direct badgap semiconductor, CZTS has strong optical absorption (absorption coefficient is above 1 x 104/cm), thus a very thin layer of film (1-2μm) can absorb over 90% of the photons over the spectrum with photon energy higher than the band gap.The optical property of the CZTS layer can be improved with a substrate temperature of 340°C.On the other hand, since Cu_xS has a direct optical band gap over the range of 1.7-2.16 eV that varies with the value of x. The higher band gap of the CZTS layer (1.99-2.09 eV) can be attributed to the Cu_xS phase. The band gap (Eg~1.5eV) of CZTS thin films with Tsub=450C is in good agreement with the experimental and theoretical values reported by other researchers.

Fig.3. Optical absorption coefficient (α) of the CZTS film as a function of photon energy (hν) for CZTS film. The film is considered to be suitable material for photovoltaic solar energy conversion if the absorption coefficient is larger than 10^5 cm^{-1} in the visible region.

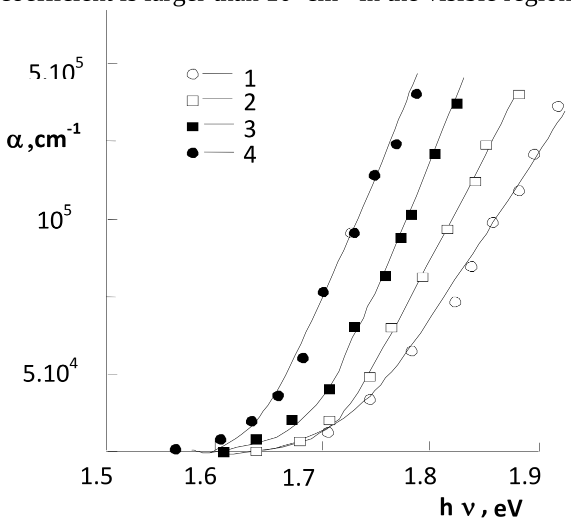


Fig.3. Optical absorption coefficient of the CZTS film

The evolution of the power conversion efficiency of CZTS-based solar cells is summarized in Figure 6. Since majority of the publications in this area have been devoted to the synthesis and characterizations of CZTS thin films, therefore this paper will review the most recent research activities of employing variable techniques for deposition of CZTS thin films. The main electrical and optical properties of the synthesized materials will be briefly discussed as well. According to the nature of the approach used for the deposition of the thin films, each category has a few subclassifications, the details of which will be shown in the following.

Electrochemical deposition is considered to be a promising technique for the low cost preparation of semiconductor thin films and has been employed for the commercial deposition of CdTe and CZTS thin film PV modules. The key for using this method is to find suitable electrochemical potential at which the metal cations can be reduced efficiently while unwanted reactions will not occur. A stacking metal layer of Cu/Sn/Zn was deposited sequentially on a TCO substrate using a three-electrode configuration where Al/Al_2O_3 was used as reference electrode. Cu and Sn was deposited at-1.14 V and -1.21 V, respectively using suitable alkaline solutions, and Zn was deposited at−1.20V in an acidic environment (pH = 5).

CdTe thin films had the best physical properties making them candidates for use in solar cell technology. We have processed a CZTS/CdTe solar cell in order to evaluate the photovoltaic efficiency. Fig. 4 shows the curves of the CZTS/CdTe cell; we use a CdTe and CdTe-HCl thin films respectively; the photovoltaic efficiency increase from 8% to 9.7%.

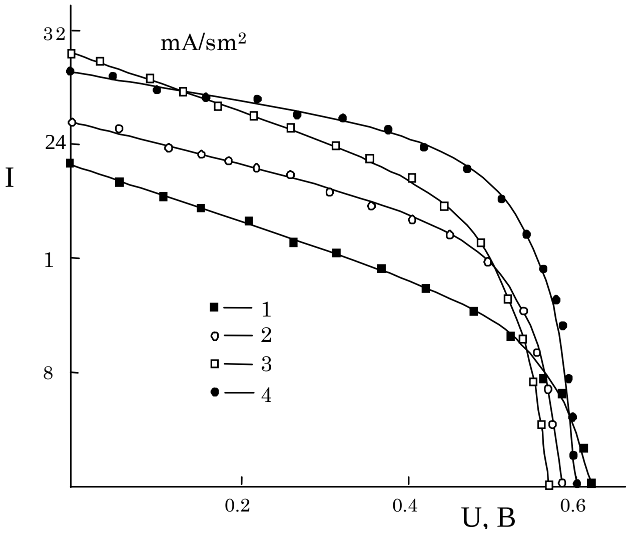


Fig.4. I-V characteristics of CZTS/CdTe solar cells just (1,2) and after (3,4) annealed, we use a CdTe (1,3) and CdTe-HCl (2,4) thin films.

IV. Conclusion

CZTS thin films were obtained by one-step electrochemical deposition at room temperature from a salt bath. Photo electrochemical characterization conducted in Na_2SO_3 solution showed that the as-deposited film behaves as a p-type semiconductor with an optical gap of about 2 eV. These preliminary findings are of value in indicating that good electro-active CZTS thin films can be successfully fabricated by a simple and cheap procedure as electrochemical deposition. The full paper containing the results using all the deposition baths tested has already been submitted. Further studies are in progress using different substrates to better investigate the effect of the thermal treatment on the performance of these materials under illumination. We obtain CdTe thin films with good physical properties, these samples can be used as window material in CdTe/CZTS solar cells to improve the photovoltaic efficiency.

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