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Physical properties of Bi doped CdTe thin films grown by CSVT and their influence on the CdS/CdTe solar cells PV-properties

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Abstract

The physical properties of Bi doped CdTe films, grown on glass substrates by the Closed Space Transport Vapour (CSVT) method, from different Bi doped CdTe powders are presented. The CdTe:Bi films were characterized using Photoluminescence, Hall effect, X-Ray diffraction, SEM and Photoconductivity measurements. Moreover, CdS/CdTe:Bi solar cells were made and their characteristics like short circuit current density (J_{sc}), open circuit voltage (V_{OC}), fill factor (FF) and efficiency (η) were determined. These devices were fabricated from Bi doped CdTe layers deposited on CdS with the same growth conditions than those used for the single CdTe:Bi layers. A correlation between the CdS/CdTe:Bi solar cell characteristics and the physical properties of the Bi doped CdTe thin films are presented and discussed.

Keywords: CdTe:Bi thin films; Physical properties; CSVT growth method; Solar cells

1. Introduction

Cadmium telluride, together with $CuIn_xGa_{1-x}Se_2$, is a very promising semiconductor material for producing large area solar cells. However the efficiency of the best CdTe-based devices has reached 16.5% [1], lower than the record efficiency of the $CuInSe_2$-based solar cells and far from the theoretical efficiency limit for cells with the CdTe band gap (~1.5 eV), around 30% [2]. For a long time, Cu has been the traditional acceptor dopant for CdTe given its high efficiency, but for CdS/CdTe solar cells it has been demonstrated that the energy conversion efficiency may be decreased when Cu is used in the CdTe layer since Cu segregates at grain boundaries. The cell performance, i. e. mainly the fill factor degrades as result of the shunting effects [3]. Cu should be avoided in the back contact to obtain a long term stable CdTe/CdS solar cell.

Therefore, the investigation for other possible doping atoms is still a challenging issue. In this line of research, recently we have demonstrated the possibility of using Bi as a doping material in CdTe [4,5]. From photoluminescence studies it has been demonstrated that changes in the emission mechanism is associated with the formation of donor and acceptor levels in the CdTe samples as a function of the Bi doping level. For the highest Bi concentration in CdTe (near 2×10^{19} cm^{-3}), a relatively low value of resistivity was reached which was approximately three orders of magnitude lower than those reported in the literature for undoped CSVT-CdTe films, while for the lowest Bi concentration (near 1×10^{17} cm^{-3}) the resistivity increased with respect to the undoped sample. These results were explained due to the fact that for low concentration of Bi, the Cadmium vacancies are occupied by Bi atoms, while for high concentration, the Bi atoms occupy Tellurium vacancies in CdTe. After this study, powders of CdTe were prepared with an even higher Bi doping level (2×10^{19} cm^{-3}). In addition, CdS/CdTe:Bi solar cells were fabricated for the first time using Bi doped CdTe powders with different Bi doping level by CSVT achieving a maximum efficiency of 8.0%, for a Bi concentration of 4×10^{17} cm^{-3}. This efficiency was lower than the highest value (12.4%) obtained by us when using the same experimental conditions for deposition of undoped CdTe films.

In this work, we study some physical and electronic properties of CdTe:Bi films with variable concentrations of Bi doping

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and their relationship with the electrical parameters obtained for CdS/CdTe:Bi solar cells, in order to evaluate the real impact of Bi doping of CdTe for this type of devices.

2. Experimental

In the first step, CdTe:Bi doped layers with variable Bi concentrations were deposited on ultrasonically clean soda-lime glass substrates by close spaced vapor-hot wall (CSVT-HW) technique starting from powders obtained by the Vertical Bridgman Method in a quartz ampoule of 20 mm in diameter, with a pyrolytic graphite coating, at a growth rate of 0.4 mm/h and a maximum temperature gradient in the solidification zone of 5 °C/cm. Bridgman ingots were synthesized from 6N Cd and Te from pure metals. Intentional doping was achieved by adding 6N Bi powder from Alfa Aesar. After this, the material was and milled up to make powders. Doping levels in all ingots were measured by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) with a mass spectrometer ELAN-6000, PE-Sciex (U.S.A), being the dopant atoms signal the most significant. Other impurities present in the different powders were K, Na, Ca and Cu, with concentrations of 10^{15} atm/cm^3, always two orders of magnitude lower than Bi concentration.

The atmosphere used during the growth of CdTe films was a mixture of Ar and O_2, with an O_2 partial pressure of 50%. In all cases, the total pressure was 0.1 Torr and prior to all depositions the system was pumped to 8×10^{-6} Torr as the base pressure. The thermal gradient between source and substrate was 200 °C. The CSVT-HW deposition of CdTe was accomplished by placing a CdTe graphite source block in close proximity (1 mm) to the substrate block. The deposition time was adjusted and the amount of ponder was previously weighted in order to obtain CdTe layers of approximately 8 μm. Thermal annealing of the films were carried on by coating with a 200 nm $CdCl_2$ layer deposited also by CSVT and then annealed at 400 °C for 30 min in air. The Bi content measured in the source powder production was used as the doping parameter of the films. Three depositions were produced for each CdTe:Bi starting material.

Solar cells were prepared by depositing CdTe films on CdS/conducting glass substrates. CdS layers of 200 nm were deposited by the CSVT-HW technique using CdS powders (of 99.99% purity), using commercial conducting glasses as substrates (0.5 μm thick SnO_2:F/glass with sheet resistivity of 10 Ω/sq). The CdS thin films were coated with 200 nm of $CdCl_2$ and then annealed for 20 min at 400 °C in air. The growth conditions of CdS were maintained constant for all the solar cells. CdTe:Bi films for the cells were deposited at the same growth conditions used for the described deposition of the CdTe:Bi layers on glass. Taking into account that the growth rate of the films depends on the substrate, previous growths were made on CdS in order to establish the growth rate for each Bi content in the powders so that in the cells the CdTe:Bi had near similar thickness. Three groups of devices were fabricated with different CdTe:Bi films. One with Bi concentration of 1×10^{17} atoms/cm^3, another with 4×10^{17} atoms/cm3 of Bi, and the third one with 2×10^{19} atoms/cm3, named samples A, B and, C respectively. For the back contact, layers of Cu and Au (2 nm and 350 nm, respectively) were evaporated, with an area of 0.08 cm^2, onto the CdTe and annealed at 180 °C in Ar. *I–V* characteristics of the CdS/CdTe:Bi solar cells were measured under simulated solar spectrum AM 1.5 (normalized to 100 mW/cm^2).

For the PL measurements we employed an Ar^+ laser focused on the sample through a cylindrical lens in order to avoid overheating of the sample. The outgoing radiation of the sample was focused on the entrance slit of a 1430-SPEX double monochromator. The detection was carried out using a thermoelectrically cooled RCA-C31034 photomultiplier tube coupled to a photon counter. The sample was attached to the cold finger of a He closed-cycle refrigeration system in order to reach low temperatures (10 K). All PL spectra were corrected for the spectral response of the system.

The crystalline structure of the films was determined by X-ray diffraction patterns with a SIEMENS D500 difractometer using Kα Co. The diffraction maxima were fitted by means of the WINPLOTR (FULLPROF_SUITE) program [6], using a P-Voigt function. For the axial texture characterization the Harris's method was employed [7–11]. The method determined the inverse pole density R_{hkl}.

Scanning Electron Microscopy images were obtained with a JEOL 6360-LV microscope. For the electrical measurements, ohmic contacts were obtained by depositing 350 nm of Au onto the CdTe:Bi layer at room temperature in the two probe configuration and annealed at 180 °C in Ar. Au leads of 0.001 in. in diameter were attached with Ag paint, and then they were encapsulated with a protective coating. Dark and illuminated room temperature resistivity measurements of the samples were carried out a using an *I–V* system coupled to a PC. In the case of illuminated resistivity measurements; a 30 W tungsten–halogen lamp was used. Finally, for spectral photoconductivity measurements, a CM110 monochromator was added to the system. During photoconductivity measurements a constant voltage of 10 V was continuously applied to samples, being the current on the sample measured as a function of the wavelength of incident light.

A step profiler was used for thickness measurements (Sloan Dektak III). Hall measurements were performance using a standard Van der Pauw geometry of contacts on the corners of a square-shaped sample. Illumination of samples during Hall measurements was performed using a light source simulating the solar spectrum. The intensity of illumination was measured using a Newport power meter (model 1815-C) with a silicon detector. All these measurements were done at room temperature.

3. Results

3.1. CdS/CdTe:Bi solar cells characterization

The values of the main parameters for the solar cells correlated to the nominal Bi concentrations are summarized in Table 1. The parameters of our best efficiency solar cell, made with undoped CdTe grown in similar conditions, are shown also for comparison.

As it can be observed, the values of J_{sc}, V_{oc} and η reach their higher values for sample B. Although the short circuit current