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Bi doped CdTe: increasing potentialities of CdTe based solar cells

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Abstract

CdTe films were deposited by closed space sublimation from different CdTe:Bi targets (from non-doped up to 0.16 at.%) previously sintered by the Bridgman method. X-ray diffraction measurements demonstrate that CdTe films are formed and Bi is incorporated. Electrical and optical characterizations show that thin films reproduce the bulk material behaviour with a decrease in resistivity and an increase in photoconductivity. Also a limit is found in the increase of photoconductivity properties versus Bi concentration.

1. Introduction

CdTe is a very important material for low cost large area photovoltaic solar cells technology, and is of great interest for flexible thin solar cells for integration in buildings and portable electronics [1]. The advantages of lightweight, effective, flexible and unbreakable modules are evident, but if solar cells also show very high stability against proton and electron radiation, they would seem to fulfil even the desires of demanding customers such as space suppliers. One of the main drawbacks of this technology is the significant gap between the performance of commercial thin film products and the theoretical highest conversion efficiency. The reported efficiency of the best small area CdTe based solar cell is 16.5%, being 7–11% for the best large area module [2], a figure far from the calculated theoretical efficiency of around 30% [3]. While some of this difference is associated with losses occurring upon integration of cells into modules, a major fraction of the gap is in the material and device quality. In this way, although several improvements have been made in CdTe/CdS solar cell technologies, such as the use of stable back and front contacts to decrease the series resistance [4, 5], other problems still await resolution. In particular p-type CdTe used as the absorber material exhibits high electrical

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resistivity and an elevated surface work function, limiting the fabrication of high efficiency solar cells. To address these limitations due to intrinsic properties of the absorber material, Cu has been used as the back contact. By using this procedure electrical resistivity is decreased due to its pseudo-Ohmic behaviour and the large diffusion coefficient of Cu. However, the main problem with using Cu contacts is that CdTe becomes doped by migration of Cu atoms on the heterojunction, degrading the performance of the solar cell [6] and leading to long term device instability [7]. To avoid Cu doping, contacts with a higher atomic radius, such as Sb and/or Mo, have been used and chemical etching in bromine methanol or PN (phosphoric acid–nitric acid) used to create a p+ region on the CdTe surface, thus decreasing the work function. Finally, alloys such as Sb₂Te₃ are being used with very good results [8]. All these efforts to improve efficiency of CdTe based solar cells have been focused on several parts of the device, but to our knowledge the CdTe layer itself has not yet been optimized, maybe due to the insufficient understanding of the intrinsic behaviour of CdTe when being doped. Very recently investigations on Bridgman grown bulk CdTe crystals demonstrated that the resistivity of single crystals can be reduced by up to four orders of magnitude with Bi concentration [9]. And what is more important, an increase in photoconductivity takes place when resistivity is decreased. Contrary to Cu, Bi atom migration is minimized, because of the fact that Bi is mainly located on Te lattice sites and thus diffusion processes are very limited [9–11]. In this work we report on the improvement of the properties of CdTe with Bi doping from the point of view of solar cell applications when CdTe is used as the absorber layer.

2. Results and discussion

Polycrystalline Bi doped CdTe films have been grown by the CSS (closed space sublimation) technique using different Bi concentrations. Bi doped CdTe powder material with concentrations of 0, 0.06, 0.1 and 0.16 at.% were previously synthesized using the Bridgman technique and then ball milled up to a uniform powder. Soda-lime glasses were used as substrates. In the CSS equipment source and substrate the thermal gradient was about 67 K mm⁻¹. All films were grown for 6 min at an Ar pressure of 6 Torr to obtain layers 3 μm thick. The temperature of the substrate and source during growth is 773 and 973 K, respectively.

One of the most interesting features for thin film CdTe solar cell applications when Bi acts as the dopant is the fact that the films present very homogeneous, compact and uniform grain sizes. In this sense, figure 1 shows a scanning electron micrograph of non-doped and 0.1 at.% Bi doped samples together with the x-ray powder diffraction spectra. As can be observed the polycrystalline nature of the film is clear, and in figure 1(a), which corresponds to undoped material, three main directions are privileged indicating a highly oriented polycrystalline film. In the case of the sample doped with 0.1 at.% Bi (figure 1(b)) some peaks appear at higher angles, indicating an increase in misorientation due to Bi doping. From the intensity of these peaks we could calculate the average grain size for each direction to be around 100 nm. It is worth noting that the Bi doped sample presents a smoother surface than does the non-doped one. This indicates that the sample quality is not affected by Bi, at least from a structural point of view, such as the film roughness.

After these interesting results concerning film quality, we investigate the electrical and luminescence properties of CdTe Bi doped films with regard to their application in solar cell technologies. In order to determine the influence of the Bi on CdTe optical transitions, photoluminescence (PL) spectra were collected at 18 K in the 1.4–1.6 eV energy range. In this study a Spectra Physics 2020-05 Ar laser was employed as the excitation source, with a 1681 0.22m Spex spectrometer coupled to a North Coast Scientific Corporation EO-817L (250 V)

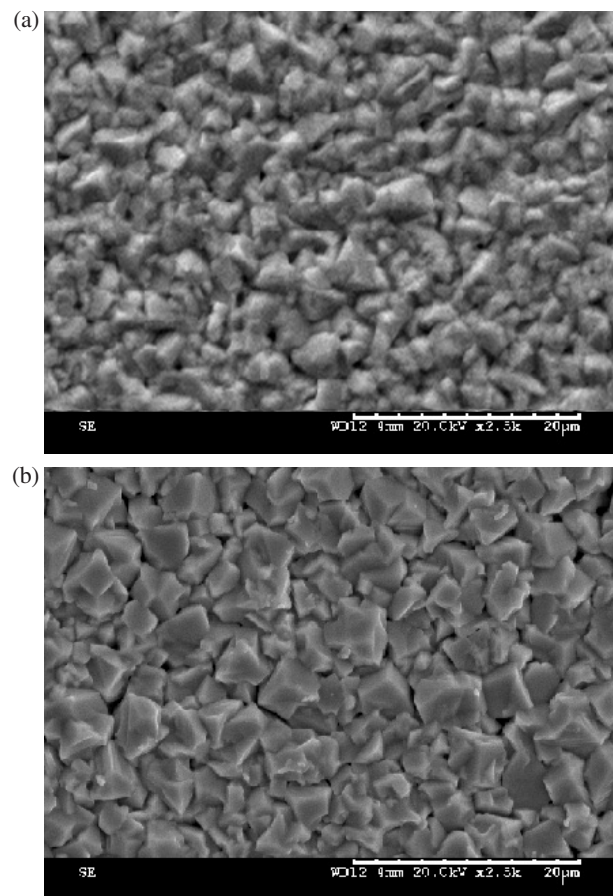


Figure 1. SEM images of undoped (a) and 0.1 at.% Bi doped (b) films.

Ge detector. The signal was collected with an EG&G 5027 lock-in amplifier. Figure 2 shows the PL spectra of undoped and 0.16 at.% Bi doped samples. It can be observed that the peak at 1.58 eV, related in CdTe to an excitonic transition bound with an acceptor, appears for both samples. When this peak appears, the crystal quality is very good as is the case for both studied compositions. As expected for CdTe related compounds, the so-called A band, related to structural defects, dominates the spectra in intensity at 1.4 eV. The presence and intensity of the A band in both cases can be explained by the high density of crystallites in the sample. For the 0.16 at.% Bi sample, the A band has been deconvoluted and a peak appears at 1.47 eV. This peak is known in the literature as the Y band; it is related to electronics levels originating from Te-atomic dislocations and to a dislocation bound exciton recombination. As can be observed in figure 2, the peak at 1.47 eV is higher for Bi doped samples suggesting a lattice distortion due to the presence of Bi. It is important to remark that size of the 1.47 eV peak depends on the Bi concentration, clearly indicating the distorting presence of the Bi ion inside the CdTe lattice.

The dark and the illuminated resistivity are the most important keys to optimizing CdTe films for solar applications as they will allow the serial resistivity of the photovoltaic device to be decreased. With this aim in mind, the dark and illuminated current–voltage characteristics were measured on the films using a Keithley 6514 system electrometer and an ET NHQ 105L

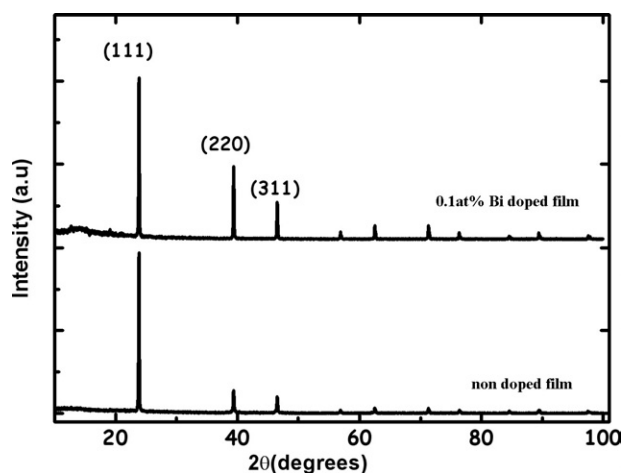


Figure 2. X-ray diffraction spectra of undoped (bottom) and 0.1 at.% Bi doped (top) films.

Table 1. Dark and illuminated resistivity together with photoconductivity gain for doping at several Bi concentrations.

Bi concentration (at.%)	Dark resistivity (Ω cm)	Illuminated resistivity (Ω cm)	Photoconductivity gain
Undoped	1.25×10^6	8.2×10^4	15.2
0.06	1.05×10^6	6.4×10^4	16.5
0.10	6.01×10^5	3×10^4	20
0.16	1.12×10^5	3.2×10^4	3.5

DC as the high voltage supply. In the case of illuminated I – V measurements, a 30 W tungsten-halogen lamp was used. Electrodes were assembled by gold deposition over the film surface, Au leads of 0.001 inch diameter were attached with Ag paint, and then they were encapsulated within a protective coating. With this system we have measured the dark and illuminated resistivity and results are presented in table 1. As can be seen, dark resistivity values decrease from $1.25 \times 10^6 \Omega$ cm for dark resistivity of undoped samples to $1.12 \times 10^5 \Omega$ cm for 0.16 at.% Bi concentration, i.e. resistivity decreases by almost an order of magnitude. These results are in concordance with those obtained on the bulk material [9]. The lowest resistivity value measured in this work is about three orders of magnitude lower than the one reported in non-intentionally doped thin films grown by the CSS method [12]. Under an illumination regime, the decrease in resistivity value saturates for 0.1 at.% Bi concentration. From these data on the electrical behaviour of Bi doped CdTe thin films we propose that Bi is a very interesting ion for improving the performance of CdTe based solar cells.

However, to assess this it is very important to look into the photoconductivity behaviour of the material. In this way, the photoconductive properties of Bi doped CdTe materials were analysed using a CM110 monochromator added to the system measuring the I – V characteristics. 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. Figure 3 shows the photoconductive response versus incident wavelength for undoped, 0.1 and 0.16 at.% Bi doped samples. As can be observed, with the exception of the intensity which is two times lower for the most heavily doped sample,

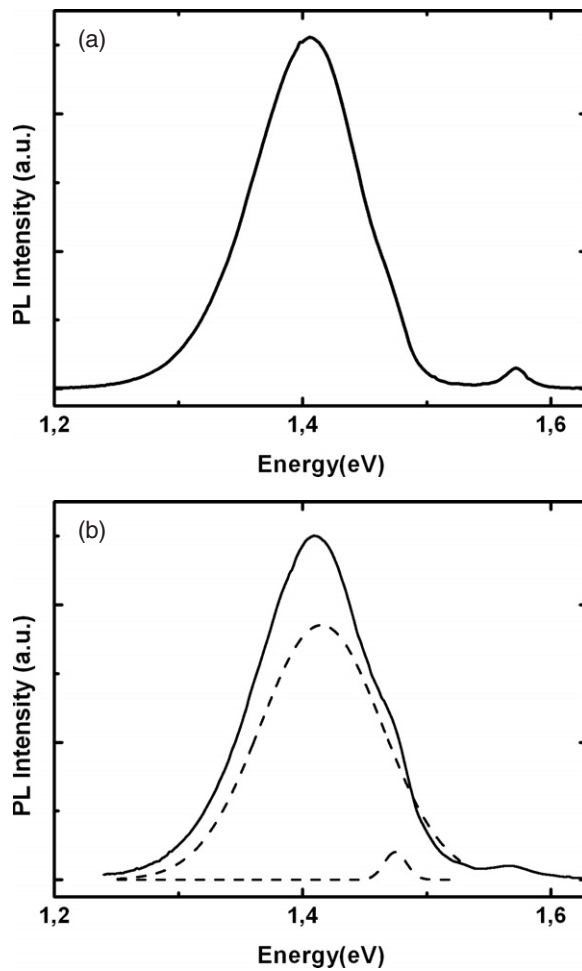


Figure 3. Photoluminescence spectra of undoped (a) and 0.16 at.% Bi doped films (b). Dashed lines indicate fitting.

the photoconductivity spectra for 0.1 and 0.16 at.% Bi are very similar. Compared with the undoped sample the spectra of doped crystals are broader, indicating a clear influence of Bi ions on the optical properties of CdTe. One of the main pieces of information we can obtain from the photoconductivity spectra in figure 4 is the fact that the 0.1 at.% Bi doped sample exhibits a photoconductive intensity comparable to that of the undoped sample, but with a broadening on both sides of the spectrum, which should allow a wider range of the solar spectrum to be collected and thus increase the photon energy collection of the final solar cell. In the case of the most heavily Bi doped sample studied in this work, the photoconductive spectrum is also broader than the undoped one, but the intensity is lower, indicating saturation of the improvements in photoconductivity induced by Bi doping. A summary of the photoconductivity gain from these measurements is also shown in table 1, where it can be observed that the photoconductivity gain increases from 15.2 to 20 for undoped and 0.1 at.% Bi doped films, while for the most heavily doped sample the gain drops drastically to very low values. These results for 0.16 at.%, together with those of electrical

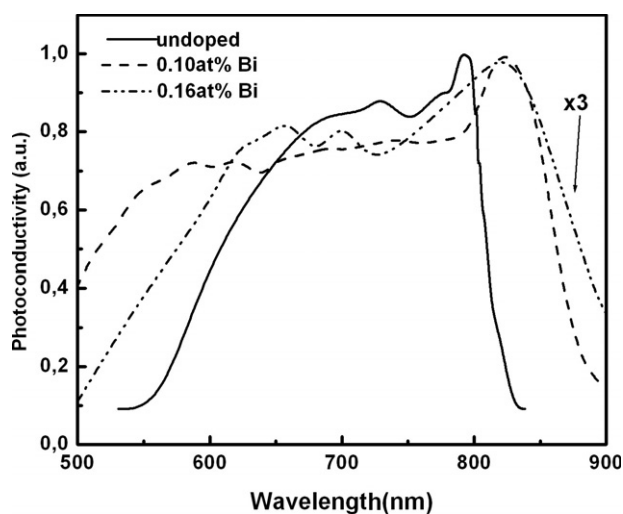


Figure 4. Photoconductivity spectra for undoped, 0.1 and 0.16 at.% Bi doped samples.

characterization, show a saturation of the photoelectrical properties of Bi doped CdTe material with a threshold at 0.1 at.% Bi concentration for solar cell applications.

3. Conclusions

In conclusion, Bi doping of CdTe polycrystalline thin films for solar cell applications is a new pathway for improving the characteristics of the absorber layer. Photoluminescence measurements have demonstrated the high crystallinity of the film microcrystallites. The presence of a 1.47 eV peak indicates that Bi has been incorporated into the CdTe film. SEM measurements show the homogeneity of the films for both undoped and Bi doped samples. Finally photoconductivity and current–voltage curves show improved values for solar cell applications, exhibiting saturation on the photoelectrical properties of the heavily doped sample. From these results, it can be concluded that doping CdTe for photovoltaic applications with Bi up to 0.1 at.% improves the properties of the basic materials and should improve the performance characteristics of devices.

Acknowledgments

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