Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 515 (2007) 6184–6187
www.elsevier.com/locate/tsf

Role of thermal treatment on the luminescence properties of CdTe thin films for photovoltaic applications

N. Armani [a,*], G. Salviati [a], L. Nasi [a], A. Bosio [b], S. Mazzamuto [b], N. Romeo [b]

[a] CNR-IMEM Institute, Parco Area delle Scienze, 37/A, 43010 Loc. Fontanini, Parma, Italy
[b] Physics Department — University of Parma, Parco Area delle Scienze, 7/A, 43100 Parma, Italy

Available online 16 January 2007

Abstract

The efficiency of CdTe based solar cells is strongly enhanced by a thermal treatment in HCF_2Cl ambient. CdTe thin films deposited on CdS/ZnO/ITO/glass by Closed Space Sublimation before and after the annealing are characterised. The CdTe morphology is studied by atomic force microscopy and scanning electron microscopy. In the treated films the non-homogeneous distribution of the grain size disappears, in addition an increasing of the dimensions of the grains is observed. Cathodoluminescence analyses show a remarkable difference in the spectra between the treated and untreated structures. A strong increase in the intensity of the 1.4 eV band is observed by increasing the HCF_2Cl content. A model of the electronic levels inside the CdTe band gap, due to incorporation of Cl (or F) is proposed.

Keywords: Solar cells; Cadmium telluride; Annealing; Luminescence; Chlorine

1. Introduction

In the recent years the efficiency of CdTe based solar cells devices has raised up to 16.5%, due to the methodical employment of post deposition heat treatment in the presence of $CdCl_2$ [1,2]. Different annealing procedures are applied by several research groups: changing the annealing temperature [3] or keeping the structures in various atmospheres like air [4] and Oxygen [5]. In all those cases an increase in the grain size is observed accompanied by an improvement of the junction characteristics: open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor. The knowledge of the effect of post deposition treatments on the device characteristics is not associated to deep information on the changes in the electronic properties of CdTe after the $CdCl_2$ treatment. Only recent studies [6] on the behaviour of Chlorine inside polycrystalline CdTe give useful results about the compensation mechanisms and the formation of complexes, already well established in the case of high quality single-crystal CdTe [7].

In the present paper the luminescence properties of CdTe films deposited by Close Spaced Sublimation (CSS) on CdS/ZnO/ITO/glass and submitted to thermal treatment in HCF_2Cl ambient are studied by SEM–cathodoluminescence (CL). The effect of HCF_2Cl on the grains of the polycrystalline materials is demonstrated by studying the morphology of the CdTe films. The CL technique provides also information, with sub-micrometric lateral resolution, on the distribution of the incorporated impurities, due to the HCF_2Cl treatment (Cl and F) inside the grains.

2. Experimental details

2.1. Preparation of the samples

The CSS is made up of a crucible containing the material to be evaporated and of a substrate very close to the crucible (2–8 mm). The deposition is performed in the presence of an inert (Ar) or reactive gas (O_2) at a pressure of 1–100 mbar. CSS technique permits to grow uniform films at a deposition rate of about 1–4 μm/min. In view of an industrial production it was found out a new method to make the Cl_2-treatment, without employing $CdCl_2$ [8]. The CdTe/CdS structure is put in an ampoule in which vacuum is done. A mixture of 100 mbar of Ar and 20 mbar of a not toxic gas containing Cl_2 such as HCF_2Cl (difluorocloromethane) is introduced in the ampoule. The temperature of the ampoule is raised to 400 °C, and an annealing of ≈5–10 min is done, after

* Corresponding author. Tel.: +39 0521269291; fax: +39 0521269206.
E-mail address: narmani@imem.cnr.it (N. Armani).

0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2006.12.080

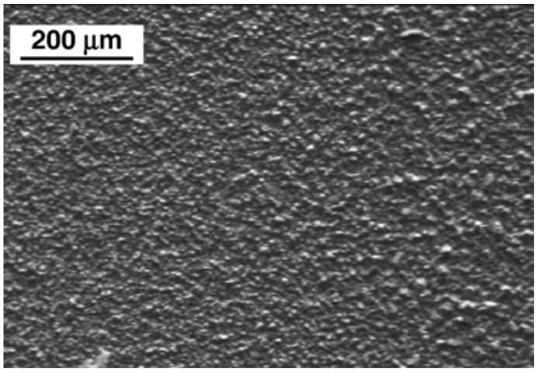

Fig. 1. Low magnification (250×) SEM image showing the non-homogenous surface of the untreated CdTe film.

which vacuum is made again. After the treatment the CdTe morphology completely changed with a size increase of the small grains. Since HCF_2Cl is decomposed at 400 °C and CdTe starts to decompose at around 400 °C, we suppose the following process happens especially for the small grains which decompose first:

$$CdTe(s) + 2Cl_2(g) \rightarrow CdCl_2(g) + TeCl_2(g) \rightarrow 2Cl_2(g) + CdTe\ (s)$$

A vacuum for a few minutes, keeping the temperature at 400 °C, is performed after the treatment in order to permit to $CdCl_2$ formed on the CdTe surface to re-evaporate and to have a clean CdTe surface ready for the back contact. The Cl_2-treatment can be made with any gas of the Freon family. The only need is that the gas contains Chlorine. This method is very effective in producing high efficiency cells. Since it avoids the use of $CdCl_2$ that could be dangerous and instead it uses a gas that is stable, inert and not toxic at room temperature. Besides it eliminates the step of $CdCl_2$ evaporation and, as a consequence, it is much more suitable for an industrial production. This process has been patented [9]. For this work some structures are submitted to a thermal treatment in the optimised conditions to obtain the higher solar cell efficiency and in conditions of excess of HCF_2Cl.

2.2. Characterisation techniques

Atomic force microscopy (AFM) is performed in contact mode by a Dimension 3100, equipped with a Nanoscope IVa controller (Veeco Instruments).

The images of the surface morphology are carried out by a Cambridge S-360 scanning electron microscope (SEM). The luminescence analyses are performed by a Gatan MonoCL system mounted on the SEM. The CL spectra as well as the panchromatic and monochromatic CL images are acquired using a dispersion system equipped with two diffraction gratings and a system of a multi-alkali (Hamamatsu) photomultiplier and an Edimburgh liquid nitrogen cooled Ge detector.

3. Results and discussion

The effect of the HCF_2Cl treatment, on the size and the homogeneity of the grains is studied by combining microscopy techniques able to depict the morphology of the CdTe surface both on a large scale and on a sub-micrometer scale. In the untreated CdTe films the non-homogeneous distribution of the grain dimensions is shown in Fig. 1. The average dimension is about 2–3 µm, but large dimension grains (up to 8 µm in diameter), appear collected in regions of several hundreds of μm^2. After the HCF_2Cl treatment, the larger grains disappear, but the average grain size increases up to about 4 µm. The CdTe surface (not shown here) results are very homogenous, demonstrating that the aforementioned recrystallisation mechanism has occurred. Concerning the single grains, their shape appears more rounded with respect to the untreated sample (Fig. 2), without the typical facets clearly visible before the annealing.

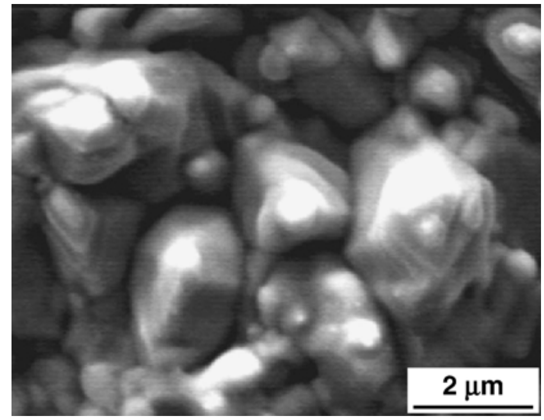

Fig. 2. SEM image of the CdTe surface of the sample HCF_2Cl treated in the optimised annealing conditions.

AFM analyses confirm, at a nanometre scale, the behaviour shown in the SEM images. The single grains of the HCF_2Cl treated CdTe studied show a terracing structure indicating the decomposition recrystallisation process occurred. By an image acquisition method based on a derivative processing of the AFM signal, the disappearing of the facets is confirmed and the

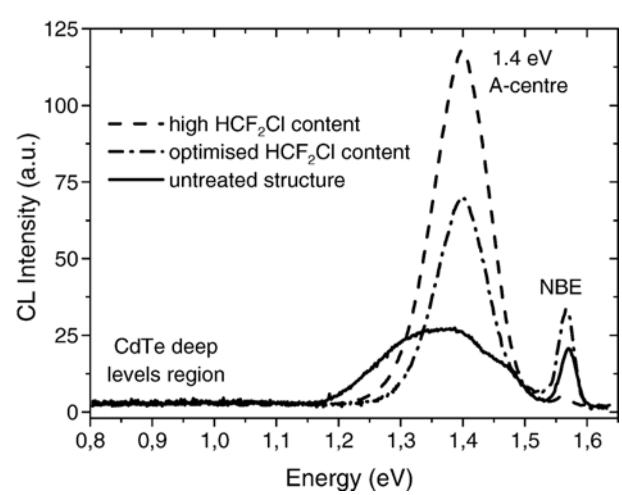

Fig. 3. Comparison among the CL spectra acquired from the CdTe film of the HCF_2Cl treated and untreated structures.