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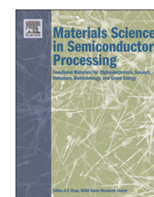

Investigation of oxide layer on CdTe film surface and its effect on the device performance

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ABSTRACT

In this work, the chemical evolution of CdTe crystal and thin film under air exposure was investigated by X-ray Photoelectron Spectroscopy (XPS). In particular, the analysis of Te 3d core level allowed us to characterize the surface oxidation. Indeed, in both cases and after a short air exposure, the Te 3d peaks exhibited clearly two components corresponding to Te–Cd and Te–O, i.e. bulk CdTe and native oxide. The later one was used to estimate an equivalent oxide layer thickness. Only a weak oxide amount could be observed on both fresh surfaces, whereas after two days of air exposure, the native oxide thickness was estimated to 2.2 nm and 0.9 nm for CdTe crystal and thin film respectively. For a longer exposition time of one month, the oxide layer thickness increased in both cases up to 7.2 and 5.9 nm, for CdTe crystal and thin film respectively. Even, if the oxidation kinetic appeared slower in the case of CdTe thin film, such insulating oxide layer formation at CdTe surface under air exposure might have negative effect on the ohmic back contact formation and further electrical characteristics of solar cells. Next to this study, aged CdTe samples were submitted to a chemical etching after several days of air exposure and before solar cell fabrication. It appeared that solar cell based on 'aged CdTe layer' after etching exhibit electrical performances similar to those obtained with a freshly elaborated CdTe device. Therefore, CdTe chemical etching appears as an effective way to remove the surface oxide layer and retrieve good cell performances. As a result, it is possible to store CdTe films for long duration before solar cells fabrication.

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1. Introduction

CdTe based polycrystalline semiconductor is one of the most popular materials for thin film solar cell manufacture [1,2]. Due to its high efficiency, low cost and high output, CdTe solar cell gains a leading role in the thin film photovoltaic technology. Indeed, the efficiency of CdTe solar cell has reached 21% at laboratory scale and 17% at industrial stage [3].

CdTe solar cells are based on a superstrate structure: Glass/TCO/CdS/CdTe/Back contact [4]. CdTe layer is usually prepared by vacuum technology, followed by $CdCl_2$ activation and surface etching [5,6]. Before metallic back contact deposition, the CdTe thin film surface may be oxidized under air exposure [7,8]. Indeed some decades ago, researchers have assumed that oxygen exposure may lead to the formation of an insulating oxide layer at CdTe surface, which might increase the electrical barrier of CdTe solar cell [9,10]. Obviously, the effect of etching is well known to avoid the negative effect of material aging and enhance the conversion performances. Nevertheless, very few insights are given in literature concerning the chemical effect of the etching step. In particular, few studies have been dedicated to oxidation kinetics and oxide thickness evaluation, which could be of useful interest for CdTe/back contact interface quality and further industrial application.

In this work, the chemical evolution of CdTe crystal and CdTe thin films were investigated by X-Ray Photoelectron Spectroscopy (XPS) in order to gain some insight on surface oxidation process under air exposure. CdTe crystal was used as a reference. The thicknesses of oxide layers were calculated with Te 3d core levels due to its sensitivity to the chemical state of oxidation. Then, devices were fabricated using 'old' and 'fresh' CdTe thin films and their performances evaluated.

2. Experimental

The oxidation under air exposure of CdTe crystal and thin film was investigated in this work. A CdTe crystal commercially

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available was used as a reference sample. CdTe thin films were elaborated by using close space sublimation as reported earlier [11]. Crystal reference surface was obtained by a 30 s dip into dilute HCl acid (1 mol/L) to remove native oxide layer on the surface just before introduction into the XPS vacuum chamber. Whereas, the CdTe thin film was freshly prepared before the XPS analysis. Then, both samples, i.e. crystal and thin film, were exposed to air first for two days and second for one month before XPS analysis.

In a last step, an aged CdTe thin film was dipped into dilute HCl acid for 30 s before the subsequent fabrication of a solar cell using standard process described in previous work [12].

XPS studies were performed using a Kratos Axis Ultra spectrometer equipped with a monochromatized Al anode X-ray source ($h\nu = 1486.6$ eV).

2.1. Oxide layer thickness calculation

The depth analyzed by XPS is directly related to the effective electron Mean Free Path (MFP) through an exponential decreasing law. The number of emitted photoelectrons I, i.e. the XPS recorded peak, at a distance d from the surface of a homogeneous material is given by the following equation [13,14]:

$$I = I_0 \times \exp\left(\frac{-d}{\lambda \sin\theta}\right) \tag{1}$$

where λ is the electron mean free path for the considered kinetic energy (in nm) and θ is the analysis take-off angle, equal to 90° for a record at normal emission, i.e. analysis perpendicularly to the surface where the bulk sensitivity is higher. The emitted electron flux I_0 generated by a bulk material without energy loss is given by

$$I_n = N_n.\ \sigma_n.\ \lambda_n.\ E \tag{2}$$

Where N is the bulk density of related element n, which can be calculated from bulk theoretical density and molecular weight of related material; λ is the inelastic mean free path (IMFP) of the appropriate photoelectrons (in nm); σ is the excitation cross section of photon and electron in the considered material and E is related to the analysis equipment.

As reported earlier for Si and III–V semi-conductors [14–17], the native oxide thickness can be evaluated from the XPS core level relative intensities of the oxide and substrate components using Eq. (1) as follows:

$$I_{semi} = I_{semi}^{\infty} \times \exp\left(\frac{-d}{\lambda \sin\theta}\right) \tag{3}$$

$$I_{ox} = I_{ox}^{\infty} \times \left(1 - \exp\left(\frac{-d}{\lambda \sin\theta}\right)\right) \tag{4}$$

$$\frac{I_{semi}}{I_{ox}} = \frac{I_{semi}^{\infty}}{I_{ox}^{\infty}} \times \frac{\exp\left(\frac{-d}{\lambda \sin\theta}\right)}{1 - \exp\left(\frac{-d}{\lambda \sin\theta}\right)} \tag{5}$$

$$d = \lambda \sin\theta \times \ln\left(\frac{I_{ox} \times I_{semi}^{\infty}}{I_{semi} \times I_{ox}^{\infty}} + 1\right) \tag{6}$$

Using Eq. (2), the bulk intensity ratio can be written as follows:

$$\frac{I_{semi}^{\infty}}{I_{ox}^{\infty}} = \frac{N_{semi} \bullet \sigma \bullet \lambda \bullet E}{N_{ox} \bullet \sigma \bullet \lambda \bullet E} = \frac{N_{semi}}{N_{ox}} \tag{7}$$

$$d = -\lambda \sin\theta \times \ln\left(\frac{1}{\frac{I_{ox}}{I_{semi}} \times \frac{N_{semi}}{N_{ox}} + 1}\right) \tag{8}$$

I_{semi} and I_{ox} represent the intensities (i.e. peak areas) of the semiconductor and oxide photoelectron peaks respectively; I_{semi}^{∞} and I_{ox}^{∞} represent the intensities of the semiconductor and oxide photoelectron peaks respectively in the case of pure bulk material; N_{semi}, N_{ox} describe the bulk densities of related element in the semiconductor and oxide respectively, λ and σ have same meaning as previously; d is the oxide thickness (in nm); θ is the electron take-off angle (with respect to the sample surface). To simplify the calculation, λ and σ have close values for CdTe semiconductor and Te oxide and can be thus considered having similar value. Therefore, the oxide layer thickness can be estimated from the relative intensities of the oxide and semiconductor components of XPS peaks using Eq. (8).

The IMFPs were calculated using the TPP-2M formula [18]. Other datas like material density and molecular weight were taken from Handbook [19]. In all experiments, the analyses were performed with a take-off angle 90°.

3. Results

3.1. XPS analysis of oxidized CdTe crystal

In order to take into account charge effects, all spectra are calibrated using the carbon C 1s core level as a reference (binding energy at 284.7 eV) [20]. The XPS survey scans of CdTe crystal, including fresh surface after HCl etching, after air exposure for two days and for one month, are given in Fig. 1. Each peak can be identified using XPS Handbook [19]. There are huge peaks associated to Cd 3d (405 eV) and Te 3d (572 eV) and a weaker peak for C 1s (285 eV) due to slight carbonaceous contamination of the surface. The O 1s peak at 532 eV appears very weak on the survey scan of fresh crystal while it is increasing and clearly identify after air exposure. The Te 3d core level peaks are clearly constituted of two components after air exposure. A more accurate analysis could be performed on core levels records as described in the following.

Fig. 2 shows Cd 3d, Te 3d and O 1s core levels spectra recorded for a CdTe crystal. For a freshly deoxidized surface, the Te $3d_{5/2}$ core level peak is located at 572.2 eV, as reported for Te element in CdTe. After air exposure, we observe clearly a peak splitting in two components located at 572.5 and 576.0 eV, associated to Te–Cd bonds in CdTe and Te–O bonds respectively [21,22]. A binding energy of 576 eV is significant for TeO_2 oxide, since in TeO_3 oxide, the Te 3d peaks are shifted to higher binding energies: 577.3 eV and 587.7 eV respectively. In addition, the intensity of oxide component is higher in Te 3d core level spectrum after one month air exposure, significant for a thicker oxide layer formation on the CdTe crystal surface. The binding energy of 405.1 eV recorded for the Cd $3d_{5/2}$ signal is in good agreement with the reported values for Cd linked to Te in CdTe material [23]. When comparing analyses on those three samples, no significant change in shape or position of the Cd 3d core level peaks is observed during air exposure, meaning that no oxidation of Cd element is evidenced. In addition, the corresponding shifts of Cd core levels are very small and below the XPS technique resolution. Thus, XPS analyses are suitable for successfully reveal Te oxide formation but not to evidence Cd oxidation.

The different chemical shifts and related intensities are gathered in Table 1. As described in experimental part, the Te oxide thicknesses were evaluated from the relative intensities of the oxide Te–O and substrate Te–Cd components of the XPS Te 3d peaks using Eq. (8). All oxide layer thicknesses are also reported in the last column of Table 1. As seen, after HCl etching step (Crystal-1), no peak related to oxide is recorded meaning that all oxide has been removed. Then, after two days air exposure, a 22 Å (2.2 nm) thick oxide layer is formed on the CdTe crystal surface (Crystal-2). A long air exposure of one month (Crystal-3) is leading to the

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