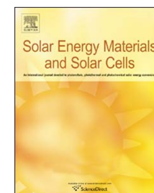
Solar Energy Materials and Solar Cells 182 (2018) 68–75

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat



Understanding arsenic incorporation in CdTe with atom probe tomography

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ARTICLE INFO

Keywords:
CdTe
As doping
Atom probe tomography
Scanning transmission electron microscopy
Molecular beam epitaxy
Single crystalline

ABSTRACT

Overcoming the open circuit voltage deficiency in Cadmium Telluride (CdTe) photovoltaics may be achieved by increasing p-type doping while maintaining or increasing minority carrier lifetimes. Here, routes to higher doping efficiency using arsenic are explored through an atomic scale understanding of dopant incorporation limits and activation in molecular beam epitaxy grown CdTe layers. Atom probe tomography reveals spatial segregation into nanometer scale clusters containing $>$ 60 at% As for samples with arsenic incorporation levels greater than 7–8 $\times 10^{17}$ cm^{-3}. The presence of arsenic clusters was accompanied by crystal quality degradation, particularly the introduction of arsenic-enriched extended defects. Post-growth annealing treatments are shown to increase the size of the As precipitates and the amount of As within the precipitates.

1. Introduction

Thin film polycrystalline Cadmium Telluride (CdTe) photovoltaics have shown exceptional promise reaching efficiencies of over 20% [1]. With the short circuit current (J_{sc}) practically at its fundamental threshold, the limiting factor in further advancing the efficiency of CdTe devices towards its theoretical limits is the open-circuit voltage (V_{oc}), which has stayed comparatively unchanged [2,3]. Increasing the p-type doping limit without compromising minority carrier lifetime is essential in overcoming this V_{oc} deficiency. Even though copper (Cu) is typically used as the p-type dopant in polycrystalline CdTe devices and high incorporation values are possible, the activation of Cu in CdTe is quite low, resulting in maximum obtainable carrier concentrations on the order of 10^{15} cm^{-3} [4].

In general, extrinsic p-type doping in CdTe can be achieved by replacing Cd with group I elements under Te-rich conditions or by replacing Te with group V elements under Cd-rich conditions. The diffusion of group I elements in CdTe is significantly faster than group V [5]. Additionally, under Te-rich environments, the Tellurium antisite (Te_{Cd}) defect is readily created and it has been shown experimentally and theoretically that the antisite defect acts as a major recombination center, therefore lowering minority carrier lifetime [6]. Thus, growth under Cd-rich conditions using group V dopants should be more favorable for increasing V_{oc}. Indeed a device made with a phosphorous (P) doped CdTe single crystal absorber, processed under Cd rich conditions, surpassed hole concentrations of 1×10^{17} cm^{-3} and yielded a $V_{oc} > 1$ V [7]. In addition to P as a potentially successful group V dopant, Density Functional Theory (DFT) calculations predicts arsenic (As) to also be a good alternative to Cu due to a similarly low defect formation energy, shallow acceptor level and lower diffusion rate [8]. While P has a lower ionization energy and predicted lower affinity for AX center formation compared to As, arsenic is considered to be a safer option for large-scale production and has a slower diffusion mechanism than phosphorous [9,10].

Arsenic doping of CdTe alloys has been an area of active research for many years, particularly for mercury cadmium telluride (HgCdTe) alloys in infrared devices [5,11–13]. However, there are many challenges associated with As doping in CdTe, especially difficulties associated with dopant activation [14,15]. As-grown films are typically highly compensating, meaning that the obvious scenario under a Cd rich growth environment for which As is primarily incorporated onto a vacant tellurium site is not the case. Post-growth annealing procedures at high temperature are necessary to properly activate the As dopants [13,16], and the mechanism for activation in CdTe is not well established. In HgCdTe, the commonly cited mechanism [17–20] for activation involves growth under a Te rich environment, prompting the amphoteric dopant, As, to sit on a Hg or Cd site. A high temperature activation anneal, typically an ampoule anneal under Te overpressure, allows As to migrate to a Te vacancy (V_{Te})site. Nevertheless, other theories for As:HgCdTe activation exist [13] including one with

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https://doi.org/10.1016/j.solmat.2018.02.023
Received 28 October 2017; Received in revised form 16 January 2018; Accepted 14 February 2018
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experimental evidence showing the formation of an $AsHg_8$ complex and As_2Te_3 glass [21–23]. Since HgCdTe is grown under Te-rich environments, the mechanism for CdTe grown under Cd-rich conditions should be different. The present study examines two annealing methods, ampoule to facilitate comparison with success in HgCdTe annealing, and rapid thermal processing (RTP) [24], a technique used frequently in semiconductor manufacturing to activate dopants, and has been used previously for CdTe samples [25].

Another problem with As activation involves the drop in net acceptor density at high incorporation levels of As [26–29] which is typically attributed to AX formation [30–33]. The AX compensating donor defect is formed by As breaking two bonds with Cd so that the As atom can move toward the neighboring Te atom and form an As-Te bond. Experimental evidence of the AX center was recently shown to most likely be the dominant donor compensating defect via thermoelectric-effect spectroscopy (TEES) [34]. An alternative or competing phenomenon could also be contributing to compensation at high As concentrations, especially approaching the solubility of As in CdTe: the formation of As-related clusters. The formation of secondary phases in CdTe has been reported previously for a limited number of dopants [35]. Duan et al., using density functional theory (DFT), suggest that the solubility of As in HgCdTe is mainly controlled by the precipitation of elemental As clusters, or under Te rich environments, an As_2Te_3 compound [36]. There are a few experimental observations that discuss the possible formation of these As-related clusters. In a CdTe sample with As concentrations of 1.5×10^{19} cm^{-3}, preliminary x-ray diffraction (XRD) data shows the possibility of As_2Te_3 formation [37]. Arsenic cluster formation associated with an As_2Te_3 glass was found to exist via extended x-ray absorption fine structure (EXAFES) in As:HgCdTe [22]. After annealing, the glass dissociated, but at higher dopant concentrations ($> 2 \times 10^{18}$ cm^{-3}), the signal was saturated by the As_2Te_3 glass or other As related clusters [38]. Clusters associated with As and H were found by SIMS ionic imaging in highly doped CdTe samples grown by MOVPE [39]. Larger As-dopant related clusters were also found via IR microscopy in a different study that may have contributed to the low level of dopant incorporation [34].

In the present investigation, atom probe tomography (APT) is employed for the direct nanoscale three-dimensional visualization of the As distribution in heavily As-doped CdTe. This is possible due to the remarkable spatial resolution and chemical sensitivity of the instrument, which has routinely investigated dopant segregation and clustering in other semiconductors [40] as well as a number of additional classes of materials. The effect of various annealing conditions on these highly doped samples is also explored. These findings will help to develop a comprehensive picture of compensation and activation in p-type doped CdTe.

2. Experimental details

As-doped CdTe samples were grown in a custom molecular beam epitaxy (MBE) system using a recipe that has previously been described [41]. Due to its negligible lattice mismatch and previous success, InSb was used as the substrate on which a 500 nm CdTe buffer layer was grown prior to the As-doped CdTe growth. A solid-source Cd_3As_2 effusion cell was used for As doping in this work, and a 20% Cd overpressure was applied to improve As incorporation [15]. As-doped CdTe layers were grown at a constant Cd_3As_2 to CdTe beam equivalent pressure (BEP) at a constant 205 °C substrate temperature. Two different annealing methods were used to activate As dopants. Ampoule annealing occurred in a sealed quartz ampoule under a Cd overpressure in a clam-shell furnace. RTP annealing occurred under an argon atmosphere with samples placed face down on a clean Si substrate.

Cathodoluminescence spectrum imaging (CLSI) was conducted on the top surfaces of films with a Horiba H-CLUE CL system in a JEOL 7600 F Schottky Field-Emission SEM. In CLSI, a full luminescence spectrum comparable to photoluminescence spectra is collected at each pixel in an SEM image. Samples were cooled to a temperature of 6 K using a continuous-flow liquid-helium cold stage (Gatan CF302). Electron-beam conditions of 5-kV accelerating voltage and 1-nA current were used, giving a generation depth of about 100–200 nm [42]. Spectra were not corrected for the CL system spectral response, and the CLSI false-color maps (explained in Supplemental info) contain 200×200 pixels.

Secondary ion mass spectrometry (SIMS) measurements were performed to compare the global As concentration profile to the nanoscale As concentration measured by APT. Atom probe specimens were prepared with an FEI Helios 600i DualBeam focused ion beam/scanning electron microscope (FIB/SEM) [43]. Final specimen radii varied between 50 and 100 nm after a 2 kV cleaning procedure to reduce gallium ion damage to roughly 2 nm on the surface. APT measurements were taken using a Cameca Instruments LEAP 4000× Si. During data collection, a charge state ratio for Cd^{+}/Cd^{2+} around 15 was maintained, typically associated with a laser energy of ~6 pJ and base temperature of ~24 K, following previous work in CdTe running parameters [44]. A 250 kHz laser pulse rate was used and a 4% detection rate could typically be achieved. Due to the relatively small amount of As in these As-doped CdTe samples, the running parameters for As-doped CdTe should not drastically differ from pure CdTe so no additional study of running parameters was performed. To more accurately calibrate the reconstructions of the APT data, transmission electron microscope (TEM) images were acquired prior to and following APT measurements using a Philips CM200 TEM [45,46]. High-angle annular dark-field (HAADF) imaging and EDS mapping was performed on an FEI Co. Talos F200X Scanning Transmission Electron Microscope (STEM) equipped with ChemiSTEM™ capabilities and operated at 200 keV.

3. Results and discussion

3.1. Arsenic dopant activation below solubility limit

3.1.1. Cathodoluminescence spectrum imaging

Epilayers with lower doping profiles, with an As concentration of about 3.5×10^{16} cm^{-3} measured by SIMS before annealing, were examined to demonstrate As dopant incorporation and activation below the solubility limit. CLSI results conducted on an As-doped CdTe sample before and after rapid thermal processing (RTP) annealing are shown in Fig. 1(a), (c) and Fig. 1(b), (d), respectively. In each figure we show an SEM image and the average CL spectrum over the entire scanned area. CLSI false color maps can be found in Supplemental info, showing uniformity across the two samples. Deviations were found at surface impurities (hillocks, debris, etc.) It can be seen that the peaks labeled 1 and 3 in Figs. 1(c) and 1(d) have similar energies. The energies of peaks 1 and 3 agree well with low-temperature photoluminescence literature values of bound exciton and DAP transitions involving As_{Te} acceptors of 1.5987 and 1.510 eV, respectively [10]. However, the relatively high intensity for peak 2 before annealing (Fig. 1(c)) is typical of undoped CdTe. In addition, distinct phonon replica for the deep donor-acceptor pair (DAP) transitions are only seen after annealing (Fig. 1(d) peaks 4 and 5). The average CL spectrum results indicate that for the annealed sample all As has been activated onto Te sites.

3.2. Visualization and analysis of As-related clustering

3.2.1. Atom probe tomography

For this study, a CdTe sample with a 5×10^{19} cm^{-3} As concentration was analyzed at various annealing conditions: unannealed, ampoule anneal, RTP at 550 °C, and RTP at 600 °C. The thickness of the As-doped layer was roughly 1 µm. The sample was then broken into multiple sections and three of these sections were annealed using different ambients, temperatures, and heating rates to compare chemical changes with electrical activation of As. One piece was annealed in a sealed quartz ampoule under a Cd overpressure in a clam-shell furnace

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