Journal of ELECTRONIC MATERIALS, Vol. 44, No. 9, 2015
DOI: 10.1007/s11664-015-3913-3

In Situ Arsenic Doping of CdTe/Si by Molecular Beam Epitaxy

S. FARRELL,[1,3] T. BARNES,[1] W.K. METZGER,[1] J.H. PARK,[2] R. KODAMA,[2]
and S. SIVANANTHAN[2]

1.—National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401, USA. 2.—EPIR Technologies Inc., Bolingbrook, IL 60440, USA. 3.—e-mail: stuart.farrell@nrel.gov

p-Type doping of the absorbed layer has been a significant challenge for CdTe solar cells. In this work, we report on *in situ* arsenic doping of molecular beam epitaxy (MBE) CdTe grown on Si(211) and the use of a cadmium overpressure to enhance incorporation. When growing CdTe:As without a Cd overpressure, extremely high As fluxes are required to achieve noticeable amounts of arsenic incorporation. By supplying a Cd flux during growth, the As incorporation increases by an order of magnitude. By including a Cd overpressure during growth, we have obtained single-crystal CdTe:As films with As incorporation concentration of 1×10^{17} cm^{-3}. An activation anneal was performed on these films in a rapid thermal annealing furnace, resulting in *p*-type layers with net carrier concentration of ~5×10^{16} cm^{-3}.

Key words: Molecular beam epitaxy, CdTe, arsenic doping, SIMS, photovoltaics, II–VI

INTRODUCTION

Polycrystalline CdTe-based photovoltaic (PV) solar cells have been very competitive in the solar market due to their low cost, nearly ideal bandgap, and high efficiency. Nevertheless, CdTe has many challenges including front- and back-contact issues, grain-boundary recombination, and difficulties in *p*-type doping. For the past two decades, hole concentration in films has been limited to 10^{13} cm^{-3} to 10^{15} cm^{-3}. Future efficiency gains will require this upper limit to be overcome without compromising minority-carrier lifetime. Consequently, we are attempting to fundamentally understand doping incorporation and activation in CdTe. In this work, we studied *p*-type doping with arsenic in molecular beam epitaxy (MBE)-grown CdTe on Si(211) substrates.

MBE of CdTe/Si has been studied for over three decades, and it has been shown to produce high-quality layers that closely approach the quality of bulk crystals.[1,2] These layers are commonly used in production of state-of-the-art mercury cadmium telluride (HgCdTe) infrared detectors. Most CdTe/Si MBE studies have focused on crystallographic quality and low dislocation density. By comparison, there have been few electrical and doping studies of MBE-grown CdTe/Si. Arsenic and other group V elements are promising *p*-type dopants for CdTe.[3] Group I elements, such as Cu, Ag, and Na, diffuse quickly and have solubility limits that induce reliability issues.[4] Experimental work has identified As as a shallow acceptor in CdTe, and it is widely used as a *p*-type dopant in mercury cadmium telluride. Several difficulties in CdTe:As growth have been noted in the past, including difficult incorporation, a tendency for crystal degradation at high incorporation, and an inability to activate As *in situ*.[5] In this paper, we present results on the incorporation and activation of As in MBE-grown films and the beneficial influence of Cd overpressure.

EXPERIMENTAL PROCEDURES

Samples were grown in a Veeco GEN930 MBE system using 3-inch Si(211) substrates. CdTe growth was performed using an effusion cell with CdTe (7 N), and doped using a Veeco Mark V 500 arsenic valved cracker. ZnTe was grown using atomic source Zn (7 N) and Te (7 N). Growth was monitored *in situ* using reflected high-energy electron diffraction (RHEED) for crystal quality and a kSA BandiT system for temperature, thickness, and surface roughness measurements.

(Received May 14, 2015; accepted June 16, 2015;

The Si(211) substrates were cleaned using a modified Radio Corporation of America (RCA) cleaning process that leaves a uniform thin oxide layer on the Si surface.[6] The substrates were then loaded into the growth chamber and the oxide was thermally desorbed at ~850°C and cooled under an As flux to ~400°C. Following this, a thin (~20 nm) ZnTe layer was deposited by migration-enhanced epitaxy (MEE) at 270°C and annealed at 330°C under a Te overpressure.[7] The substrate was then allowed to cool for 30 min to 200°C for CdTe growth.

A CdTe buffer layer was grown to thickness of 1 μm to 5 μm to avoid arsenic interacting with the region of high dislocation density near the CdTe/ZnTe/Si interface. CdTe growth was performed at a rate of ~1 μm/h and was usually subjected to an *in situ* annealing cycle for every micron of growth to improve crystal quality and reduce dislocation density.[2]

Arsenic doping was performed after the initial buffer layer was grown. The As flux was controlled by a valve in the cracker cell while keeping the bulk and cracker temperatures constant at 1000°C and 300°C, respectively. Cadmium overpressure was achieved using an effusion cell with elemental Cd.

Samples were characterized using x-ray diffraction for crystal quality and secondary-ion mass spectrometry (SIMS) for As concentration. Arsenic activation was achieved via either ampoule anneals or in a rapid thermal annealing (RTA) system. For ampoule anneals, samples were sealed in an evacuated quartz ampoule with a small quantity of Hg or Cd (~200 mg) for overpressure and annealed in a clam-shell furnace at 450° to 500°C for 10 min to 20 min. RTA anneals were performed in argon atmosphere with the samples placed face down on a clean Si, quartz, or glass substrate, annealing for 10 min to 20 min at 400°C to 500°C. Electrical characterization was performed using Hall measurements or capacitance–voltage (C–V) measurements depending on whether the Si substrate was undoped ($\rho > 20\,\Omega$ cm) or p^+-doped ($\rho \leq 0.005\,\Omega$ cm), respectively.

RESULTS AND DISCUSSION

To examine the As incorporation in the CdTe films, samples were grown using stepped structures for SIMS analysis. Beam flux measurements were performed using a nude ion gauge. A beam equivalent pressure (BEP) of ~7.5 × 10^{-7} torr was typically measured for the CdTe growth source; this equates to a growth rate of ~1 μm/h. Figure 1 shows the results of adding a 20% (1.5×10^{-7} torr) cadmium overpressure for different arsenic fluxes. The detection limit for As in CdTe is in the range of mid 10^{14} cm^{-3} to low 10^{15} cm^{-3}. There was a noticeable increase in As incorporation when the As flux was first added at around 1.4 μm; although the data are noisy for low As concentration, the effects of the Cd overpressure become clearly visible for incorporation densities $> 10^{16}$ cm^{-3}. Figure 2 shows a zoomed-in view of the final three steps in this structure, and the average incorporation for each step of the structure. The addition of a 20% Cd/CdTe overpressure clearly

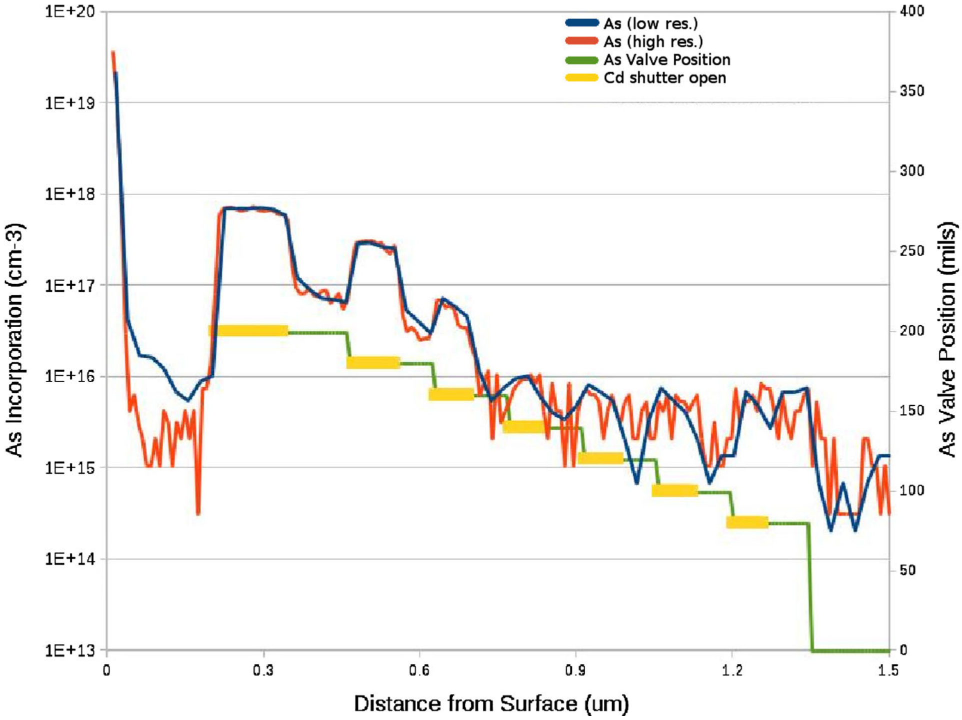

Fig. 1. As incorporation profile (blue for low resolution, orange for high resolution) from SIMS on a CdTe layer. The right-hand axis indicates the As cracker valve position (green line), which is proportional to the BEP. The lighter (yellow) portions indicate regions where the Cd shutter is open (Color figure online).

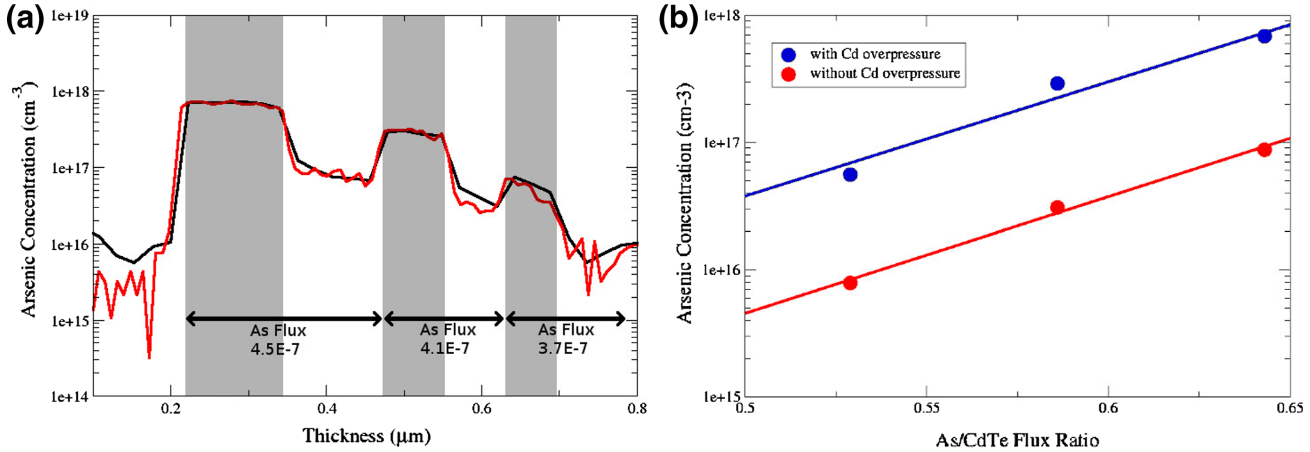

Fig. 2. Analysis of SIMS data shown in Fig. 1: (a) zoomed view of the final three steps where the darker regions have a Cd overpressure, and (b) correlation of arsenic incorporation with the flux used during growth.

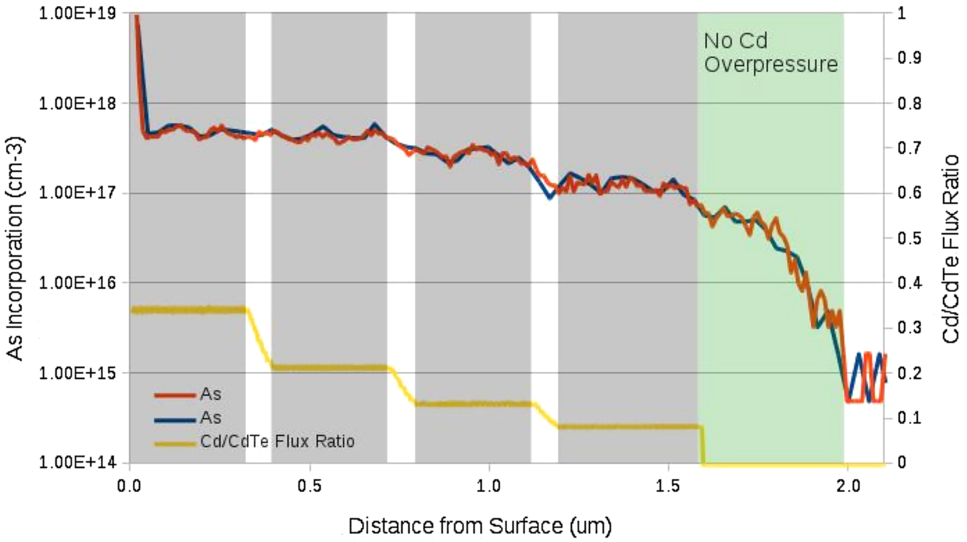

Fig. 3. As incorporation profile (blue for low resolution, orange for high resolution) from SIMS on a CdTe layer. The right-hand axis indicates the Cd/CdTe flux ratio as measured by BEP (yellow line), with the darker regions highlighted corresponding to a steady Cd overpressure (Color figure online).

increased the As incorporation by an order of magnitude (Fig. 2b). The As incorporation shows a strong linear dependence with the As flux with or without the presence of a Cd overpressure. This suggests that the additional Cd overpressure increases the effective sticking coefficient by roughly an order of magnitude.

To further characterize the effects of Cd overpressure on As incorporation, two samples were grown with a step structure of incrementally increasing Cd overpressure. The sample in Fig. 3 shows the As incorporation as the Cd overpressure was varied from zero to 35% under a steady As flux. A noticeable increase in the As concentration can be observed when the Cd flux was added to the growth. The incorporation continued to increase as higher Cd flux was added to the layer. There appears to be a saturation of the As incorporation as the Cd flux ratio was increased from 20% to 35%. This is confirmed by the analysis of a second sample in Fig. 4, which shows the results of higher Cd overpressure. No noticeable increase of the arsenic concentration was observed when the Cd/CdTe flux ratio was increased from 30% to 50%. The increased incorporation observed for a 75% overpressure coincided with a decrease in crystal quality as observed by RHEED. Subsequent attempts to grow As-doped layers using a Cd overpressure in the range of 35% to 50% exhibited a RHEED pattern with indications of twinning shortly after initiating As doping. As the thickness of these layers increased, the surface became exponentially rougher after 2 h to 3 h of growth, as observed by the intensity of light scattering from the sample surface. Analysis of samples showing a similar breakdown in crystal structure by atom probe tomography revealed the existence of

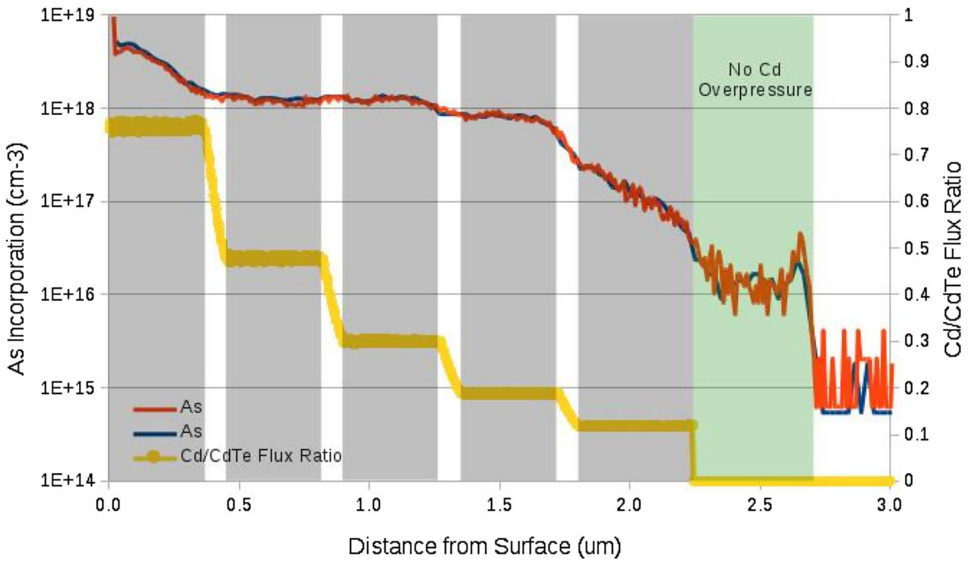

Fig. 4. As incorporation profile (blue for low resolution, orange for high resolution) from SIMS on a CdTe layer. The right-hand axis indicates the Cd/CdTe flux ratio as measured by BEP (yellow line), with the darker regions highlighted corresponding to a steady Cd overpressure (Color figure online).

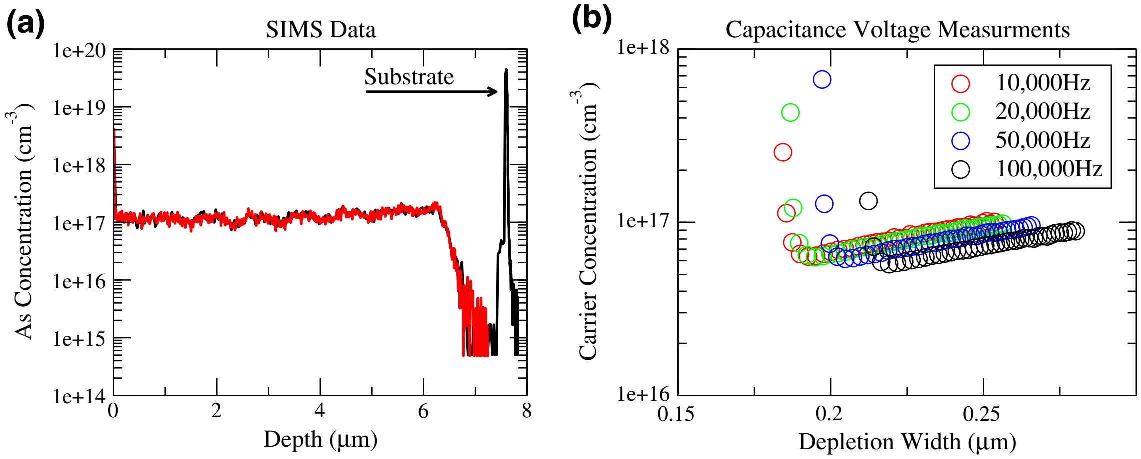

Fig. 5. An arsenic-doped layer grown with 20% Cd overpressure on a *p*-type silicon substrate: (a) SIMS profile of arsenic incorporation, and (b) capacitance–voltage measurement after the sample was annealed in an RTA system at 525°C for 10 min.

5-nm to 20-nm As_2Te_3 inclusions. It is believed that excess Cd overpressure causes formation of defects in which these inclusions form. The inclusions then nucleate amorphous or polycrystalline growth in their vicinity. This is a likely cause of the runaway effect observed by Park et al.[5] where increasing As incorporation is due to proliferation of As_2Te_3 inclusion rather than As into the regular crystal lattice. Because the arsenic is bound into stable particles rather than as substituents or interstitials, an activation anneal is unable to force them into an As_{Te} dopant position.

Figure 5a shows the SIMS profile of a thick CdTe:As layer grown on highly doped *p*-type silicon. A 1 μm buffer layer was grown to ensure reasonable crystal quality prior to the introduction of As. Doping for this sample was performed using a 20% Cd overpressure and a 0.55 As/CdTe doping flux. As a result, steady As incorporation of 1×10^{17} cm^{-3} was obtained for a 6 μm film; no runaway effect or crystal degradation was observed. Despite being present in the as-grown crystal, arsenic is inactive as a dopant and requires an activation step.

To achieve *p*-type doping, an *ex situ* activation anneal is required. For HgCdTe, this is typically done by sealing the samples in a quartz ampoule with a small amount of Hg to provide an overpressure which helps preserve the sample surface and allows for a vacancy fill anneal. We performed many of our activation anneals using an RTA furnace in addition to the more traditional closed ampoule anneals using either a Cd or Hg overpressure. For annealing in the RTA, samples were placed between two pieces of thin, alkaline-free technical glass in the furnace. By placing the sample surface in contact with the glass, we were able to perform relatively high-temperature anneals while maintaining the surface morphology. In contrast, layers that were annealed uncovered were destroyed at temperatures in excess of 300°C. The samples were heated with a linear ramp to a set point of 525°C in 30 s, annealed for 10 min, then allowed to cool to room temperature over 5 min. A Schottky diode was formed by pressing an indium dot to the surface of the sample, and the carrier concentration was then determined by C–V measurements. The results in Fig. 5b indicate a carrier concentration of $\sim 5 \times 10^{16}$ cm^{-3}, which corresponds to about 50% activation. This is similar to other findings in the literature.[5]

CONCLUSIONS

We performed a detailed MBE investigation on the effects of Cd overpressure on *in situ* arsenic doping of CdTe layers. By applying a 20% Cd overpressure, arsenic incorporation could be increased by roughly an order of magnitude while maintaining a steady doping profile in the layer. Use of an overpressure >20% showed diminishing returns. Incorporation densities as high as 1×10^{18} cm^{-3} were observed in test structures, and 1×10^{17} cm^{-3} has been observed for thick layers. Postgrowth activation anneals of these layers are necessary to activate the dopant and were performed in an RTA furnace. Activation efficiencies of ~50% were measured. These results indicate that CdTe films can be doped with As and activated to obtain carrier concentrations in excess of 1×10^{16} cm^{-3}. Executing this in polycrystalline films would be sufficient to overcome historical open-circuit voltage barriers and boost CdTe solar cell efficiency well beyond that of polycrystalline Si.

ACKNOWLEDGEMENTS

The work was support by the US Department of Energy under Contract No. DE-AC36-08-GO28308 with the National Renewable Energy Laboratory. SIMS measurements were provide by Dr. A. Wang at Evans Analytical Group.

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