Incorporation and activation of arsenic in MBE grown HgCdTe


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ABSTRACT

Research into P-type doping of HgCdTe with arsenic has concentrated on the use of a conventional effusion cell and optimisation of growth conditions to achieve an increase in incorporation efficiency. This study investigates the use of a cracker cell, which is now the preferred method of doping HgCdTe due to its higher arsenic incorporation efficiency under optimum growth conditions. A detailed investigation of a number of arsenic doped HgCdTe layers grown on CdZnTe substrates by Molecular Beam Epitaxy (MBE) using a cracker cell as a source of arsenic is presented. Growth parameters influencing the amount of arsenic incorporated, such as the cracker-cell bulk temperature and substrate temperature, were investigated. Arsenic depth profiles were obtained via detailed Secondary Ion Mass Spectrometry (SIMS) where all major constituents in the epilayers were analysed. Magneto-transport Hall measurements were performed on as-grown material and those that underwent high temperature anneals typical for arsenic activation. Using the Quantitative Mobility Spectrum Analysis (QMSA) technique, contribution to total conductivity arising by various carriers present in the samples have been separated. As-grown samples were found to exhibit n-type behavior consistent with arsenic incorporating on cation sublattice, while samples that underwent high temperature annealing show partial activation of arsenic with electron compensation.

INTRODUCTION

Today’s high performance HgCdTe infrared focal plane arrays require the ability to accurately control the material doping type and level during MBE growth. While indium is now a standard n-type dopant used in the growth process, p-type doping of HgCdTe with arsenic (As) remains a challenging problem primarily attributed to the amphoteric behaviour of As, low sticking coefficient and its low activation at growth temperatures. In contrast to liquid phase epitaxy (LPE) or metal-organic vapor phase epitaxy (MOCVD), optimum conditions for MBE growth of HgCdTe occur only under Te-saturated conditions, implying that more cation vacancies exist as compared to Te vacancies [1]. This has commonly resulted in n-type conductivity in as-grown arsenic doped samples, with general acceptance that the incorporated arsenic preferentially occupies the available metallic sublattice sites, hence acting as donors in the material [2]. For p-type conductivity, arsenic should reside predominantly on the Te anion sublattice sites. In this study, an arsenic cracker cell is utilized during MBE growth to investigate the incorporation of arsenic in HgCdTe and its dependence on substrate growth temperature and arsenic bulk/cracker zone cell temperatures.
<table>
<thead>
<tr>
<th>Growth</th>
<th>Sample</th>
<th>Thickness</th>
<th>Arsenic Bulk</th>
<th>Cracker</th>
<th>Substrate Temp</th>
<th>x (FTIR)</th>
<th>x (SIMS)</th>
<th>SIMS (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MCT80</td>
<td>10.4 µm</td>
<td>300 °C</td>
<td>400 °C</td>
<td>184.5 °C</td>
<td>0.310</td>
<td>0.304</td>
<td>7.5 × 10$^{17}$</td>
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<td></td>
<td>MCT81</td>
<td>9.6 µm</td>
<td>300 °C</td>
<td>650 °C</td>
<td>184.5 °C</td>
<td>0.360</td>
<td>0.389</td>
<td>6.0 × 10$^{17}$</td>
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<td>2</td>
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<td>8.9 µm</td>
<td>300 °C</td>
<td>400 °C</td>
<td>181 °C</td>
<td>0.322</td>
<td>0.317</td>
<td>2.81 × 10$^{16}$</td>
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<td></td>
<td>MCT97</td>
<td>8.9 µm</td>
<td>250 °C</td>
<td>500 °C</td>
<td>182 °C</td>
<td>0.333</td>
<td>-</td>
<td>5.7 × 10$^{15}$</td>
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<td>MCT98</td>
<td>8.9 µm</td>
<td>275 °C</td>
<td>500 °C</td>
<td>180 °C</td>
<td>0.321</td>
<td>-</td>
<td>1.45 × 10$^{16}$</td>
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<td></td>
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<td>9.4 µm</td>
<td>280 °C</td>
<td>500 °C</td>
<td>182 °C</td>
<td>0.333</td>
<td>0.335</td>
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<td>250 °C</td>
<td>600 °C</td>
<td>182 °C</td>
<td>0.295</td>
<td>0.314</td>
<td>4.5 × 10$^{16}$</td>
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<td>MCT107</td>
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<td>300 °C</td>
<td>600 °C</td>
<td>182 °C</td>
<td>0.325</td>
<td>0.330</td>
<td>1.5 × 10$^{18}$</td>
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<td>MCT108</td>
<td>10.1 µm</td>
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<td>600 °C</td>
<td>182 °C</td>
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<td>280 °C</td>
<td>500 °C</td>
<td>182 °C</td>
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<td>0.294</td>
<td>2.4 × 10$^{16}$</td>
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<td></td>
<td>MCT113</td>
<td>5.9 µm</td>
<td>260 °C</td>
<td>700 °C</td>
<td>182 °C</td>
<td>0.369</td>
<td>0.349</td>
<td>4.0 × 10$^{17}$</td>
</tr>
<tr>
<td></td>
<td>MCT114</td>
<td>6.8 µm</td>
<td>280 °C</td>
<td>650 °C</td>
<td>182 °C</td>
<td>0.358</td>
<td>0.366</td>
<td>5.6 × 10$^{17}$</td>
</tr>
</tbody>
</table>

**TABLE I**

HgCdTe samples grown (tabulated in order of growth) under varying conditions in 3 separate growth campaigns. Note that Hg flux was kept constant for each campaign.

Relatively few studies [3] have been published on the use of a cracker cell for arsenic incorporation and resulting electrical activity in HgCdTe. While it is well known that As$_2$ dimers have higher sticking coefficient than As$_4$ tetramers, it was Almeida who showed that the use of a cracker cell resulted in significantly higher incorporation rates [4]. This means that less arsenic flux will be required to achieve a desired dopant level, reducing the amount of background impurities in the chamber.

**EXPERIMENTAL PROCEDURES**

A number of arsenic doped HgCdTe single layers were grown on (211)B CdZnTe substrates with different compositions under varying arsenic bulk and cracker cell temperatures in a Riber 32 MBE growth system located at the University of Western Australia. The substrates were purchased from Nikko Materials Co. Ltd with a nominal 4% Zn concentration and dimensions of 10 mm × 10 mm × 0.8 mm. The arsenic flux introduced during the growth was regulated by a standard dual-zone Veeco valved arsenic cracker cell where the needle valve was adjusted to allow approximately 70-80% of the maximum flux into the chamber. SIMS analysis on the bulk of the samples used in this study was performed at the Australian Nuclear Science and Technology Organisation (ANSTO) on a Cameca IMS 5f Dynamic SIMS system utilising reference samples as analysed by the Evans Analytical Group (EAG) using the AsCs$^+$ method [5]. Comparison of several reference standards reveals a difference of $\approx \pm 50\%$ between SIMS analyses performed by Evans Analytical & ANSTO. The depth of the SIMS crater was measured using an Alpha-Step IQ surface profiler. The Cd and Te isotopes were also monitored to allow for determination of the cadmium mole fraction in the sample. SIMS on as-grown samples indicate successful incorporation of As ranging from $8 \times 10^{15}$ cm$^{-3}$ to $1.5 \times 10^{18}$ cm$^{-3}$ as indicated in Table I. Optimum growth conditions were ensured with the use of in-situ reflection high energy electron diffraction (RHEED) to monitor growth from beginning of nucleation to end of growth. The x mole ratio and thickness of each sample was determined via Fourier Transform Infrared (FTIR) measurements performed on a SOPRA GESS5 ellipsometer at room temperature.

The samples shown in Table I were accumulated from 3 separate growth campaigns. For investigating the effect of high temperature annealing, several doped layers (MCT107, MCT108 & MCT114) were annealed isothermally at $\approx 430$ °C for
Fig. 1. Arsenic concentration (thick line) and Cd composition (dashed line) from SIMS measurement of MBE grown HgCdTe. The substrate temperature was varied in increasing steps of 3 °C from 176 °C to 185 °C while keeping other growth conditions constant.

about 10 mins followed by the standard n-type anneal of 250 °C for 24 hours [3]. Variable temperature (40 K to 300 K) magneto-transport Hall measurements up to a magnetic field of 12 T coupled with Quantitative Mobility Spectrum Analysis (QMSA) [6] were used to extract the nominal carrier concentrations and carrier mobilities of the as-grown and annealed samples.

RESULTS AND DISCUSSION

Arsenic incorporation

The SIMS results indicated successful incorporation of arsenic in HgCdTe and good uniformity in the grown layers. As the needle valve was adjusted manually to approximately the same position before every growth run, slight variations in the amount of arsenic incorporated were observed for samples grown under the same conditions. An arsenic spike close to the HgCdTe/CdZnTe interface is observed on all samples analysed and may be attributed to the change in crystal matrix composition near the interface which may affect the SIMS analysis. A sample was grown under varying substrate temperatures to study the effect of substrate temperature on arsenic incorporation (see Figure 1). A clear decrease in arsenic incorporation with increasing substrate temperature for a fixed bulk/cracker cell temperature was observed. Note that arsenic incorporation is more sensitive at the higher substrate temperatures where a change of 3 °C from 182 °C to 185 °C led to a drop in the concentration of arsenic by a factor of almost 7 times. Also note the relatively insignificant change in composition of the material (within ±0.01) as a function of the growth temperatures used here. This indicates that changing the doping level during growth via substrate temperature modulation is viable without interrupting the homogeneity of the growing HgCdTe epilayer.

A number of samples were also grown with fixed bulk temperatures and varying cracker temperatures. The SIMS results suggest that as the cracking zone temperature is increased, there is a higher incorporation of arsenic in the layers verifying the higher sticking coefficient of As₂ dimers. This is evident from Table I by comparing the 2 samples, MCT80 and MCT81.
where an increase in cracker cell temperature of 250 °C led to an increase in arsenic concentration of almost two orders of magnitude. A similar trend was also observed between samples MCT97 and MCT102 as well as MCT109 and MCT111 where a change of 100 °C led to an order of magnitude increase in As incorporation. Also as expected, samples grown under the same cracking zone temperature but higher bulk temperature have higher arsenic concentrations due to a higher flux emanating from the cell. It was observed that a 20 - 30 °C increase in bulk zone temperature is sufficient to increase arsenic incorporation by an order of magnitude (between samples MCT111 & MCT107, MCT97 & MCT100). Analyzing the table further, it is apparent that the bulk and cracker cell temperatures used in this study were far from optimal and may be further improved by utilizing lower bulk cell and higher cracker cell temperatures (as in the case of MCT113) to achieve a desired doping level. It is also important to state that there were no significant differences in arsenic incorporation levels as a function of composition for the samples investigated in this study.

Aside from determining arsenic concentrations in the sample, SIMS was also used to obtain the composition (x value) by monitoring the 106Cd and 123Te isotope ion counts as a function of depth through the HgCdTe epilayer and the substrate. The above isotopes are in lower abundance compared to their respective other natural occurring isotope counterparts, but were chosen as they provided yields which consistently fall within the electron multiplier range of the SIMS equipment. This condition ensures a more consistent and reliable comparison between individual sample SIMS profiles. A simple relationship between the composition of the material and the ion yields is based on the following equation [7]

\[
x = \gamma_{sub} \frac{133Cs^{106Cd^+}}{133Cs^{123Te^+}}
\]

where

\[
\gamma_{sub} = \frac{x_{sub}}{\frac{133Cs^{106Cd^+}_{sub}}{133Cs^{123Te^+}_{sub}}}
\]

and \(x_{sub}\) used here is 0.9. This value of 0.9 assumes that the Cd\(^+\) and Te\(^+\) ions yield in the substrate is equivalent to the yield that would be obtained from a Hg\(_{0.1}\)Cd\(_{0.9}\)Te layer. Calculated average values for the composition from SIMS analyses are shown in Table I. Comparing the values obtained from FTIR indicate that the values obtained from SIMS using this method are relatively similar with a maximum 8% difference for all the samples investigated here, making SIMS a viable technique for \(x\) mole ratio determination from a single SIMS measurement without requiring a reference standard.

**Arsenic activation**

It has been widely reported in the literature that arsenic, as with most group V elements, is an amphoteric dopant in HgCdTe where it can reside in both the metallic and non-metallic sublattice sites acting as donors and acceptors, respectively [8]. Coupled with the added complexity in interpretation of Hall data commonly encountered for p-type HgCdTe [9], the extraction of carrier transport properties can be a difficult process. 8-contact Hall bars were fabricated and used as test structures for the magneto-transport Hall measurements. The use of high field Hall measurements and QMSA is important in analysing p-type HgCdTe where anomalous field dependencies are commonly observed. The QMSA algorithm [10] is applied as a multi-carrier fitting (MCF) method on the raw Hall data to extract individual carriers’ transport properties in a mixed conduction system. A
summary on the interpretation of the conductivity mobility spectra as output from QMSA may be found in reference [11]. Figure 2 shows the mobility spectrum at 77 K for sample MCT107, as-grown and after annealing with the percentage contribution of the different carriers to overall conduction indicated. It is evident from the high mobility electron peak (which contributes more than 90% to total conductivity) in Figure 2(a) that at 77 K, the as-grown material with arsenic doping level of \( \approx 1.5 \times 10^{18} \text{ cm}^{-3} \) (see Table I) is predominantly n-type with an electron carrier concentration of \( 9.5 \times 10^{15} \text{ cm}^{-3} \) and mobility of 17,000 cm\(^2\)/V.s. This difference of almost 2 orders of magnitude between arsenic concentration and extracted electrical activity suggests that the bulk of arsenic incorporates mainly as some form of neutral complex. These results are consistent with an electronic quasichemical statistical model using energies deduced from \textit{ab-initio} calculations developed by Berding and Sher that predicts the majority of arsenic incorporates on the cation sublattice sites and should be n-type, but a large fraction of this arsenic is bounded to a mercury vacancy to form a neutral complex, \( \text{As}_{\text{Hg}}^{-} \text{V}_{\text{Hg}} \) [12].

For annealing, a piece of MCT107 and a small amount of Hg were placed in a vacuum sealed quartz ampoule, allowing annealing under Hg over-pressure in a well profiled dual zone furnace. The ampoule was placed into the furnace in such a way that the Hg source was always kept at a few degrees cooler than the sample during the anneal, to prevent Hg from condensing on the sample at any stage. For arsenic activation, the sample was annealed isothermally at a temperature of 430 °C for 10 mins followed by the standard anneal at 250 °C for 24 hours to remove Hg vacancies [13]. The high temperature anneal step is necessary to increase the number of Hg vacancies present and supply enough thermal energy for arsenic to move to the appropriate anion sites. Theoretical models discussing the importance of Hg vacancies and their participation in the movement of arsenic during the activation anneal can be found in [14], [15].

Hall effect measurements on the annealed sample (see Fig. 2(b)) indicate that the sample is p-type at 77 K with a hole concentration of approximately \( 3 \times 10^{17} \text{ cm}^{-3} \) and a hole mobility of around 231 cm\(^2\)/V.s. However, this accounts for only...
about 20% of arsenic present in the material. Furthermore, an element of compensation remains with the holes contributing only around 48% to the total conduction and another electron species observed to contribute about 44%. This electron peak was calculated to have a carrier concentration of $1.9 \times 10^{16}$ cm$^{-3}$ and an electron mobility of around 3,000 cm$^2$/V.s at 77 K. A possible explanation of this peak may be due to a degenerate inversion layer commonly found on the surface of p-type HgCdTe. However, this surface carrier density of $\approx 1.6 \times 10^{13}$ cm$^{-2}$ (using $n_{2D} = n_{3D}/d_{sample}$) is an order of magnitude higher than which was previously observed (typically $\approx 10^{11} - 10^{12}$ cm$^{-2}$) indicating that the electron species may truly be a bulk effect and unlikely a surface effect. At this time, the nature of these carriers is speculated to be due to structural defects caused by the high temperature anneal acting as donors in the material but is still a subject of investigation.

Figure 3(a) and 3(b) show the full temperature dependence of carrier concentration and mobilities for the previously discussed MCT107, as well as two additional as-grown arsenic doped layers, MCT108 & MCT113. All samples exhibit strong n-type conduction, and show increasing electron concentration with increasing arsenic doping level. This confirms that arsenic is contributing to the n-type conductivity of the sample rather than the conductivity being due to other defect species. In all three samples, the extracted electron carrier concentration is approximately 2 orders of magnitude less than the arsenic doping level in the material, reinforcing the earlier assumption that arsenic incorporates primarily as some form of neutral complex during MBE growth. While the arsenic concentrations in MCT107 and MCT108 are similar, their mobilities differ, with MCT108 being a factor of $\approx 1.8$ higher, consistent with the classical dependence of electron mobility with composition of the HgCdTe since MCT108 has lower x value [16]. The electron mobilities exhibit a $T^{-\alpha}$ temperature dependence in the range 140 to 300 K where $\alpha$ is between 0.92 and 1.1 as indicated for the 3 samples in Figure 3(b). Figure 4(a) and 4(b) show the full temperature dependence of carrier concentration and mobilities for MCT108 after being annealed under the same conditions as described for MCT107. The results show that arsenic was once again partially activated with the annealed sample having a hole concentration of $1.05 \times 10^{17}$ cm$^{-3}$ and a mobility of 358 cm$^2$/V.s at 77 K. From the hole temperature dependency, an
Fig. 4. Extracted carrier concentrations and temperature dependency of holes and electrons extracted from iQMSA for MCT108 after activation anneal.

TABLE II

<table>
<thead>
<tr>
<th>Sample</th>
<th>x</th>
<th>SIMS</th>
<th>As-grown (77 K)</th>
<th>After Anneal (77 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCT107</td>
<td>0.33</td>
<td>1.5 × 10^{18} cm^{-3}</td>
<td>n - 9.4 × 10^{15} cm^{-3}</td>
<td>p - 3 × 10^{17} cm^{-3}</td>
</tr>
<tr>
<td>MCT108</td>
<td>0.27</td>
<td>1.3 × 10^{18} cm^{-3}</td>
<td>n - 7.5 × 10^{15} cm^{-3}</td>
<td>p - 1.05 × 10^{17} cm^{-3}</td>
</tr>
<tr>
<td>MCT113</td>
<td>0.37</td>
<td>4 × 10^{17} cm^{-3}</td>
<td>n - 2.5 × 10^{15} cm^{-3}</td>
<td>N/A</td>
</tr>
<tr>
<td>MCT114</td>
<td>0.36</td>
<td>5.6 × 10^{17} cm^{-3}</td>
<td>N/A</td>
<td>p - 1.22 × 10^{17} cm^{-3}</td>
</tr>
</tbody>
</table>

activation energy of 5.5 meV was calculated using the temperature range 40 K to 100 K indicating that arsenic is a shallow dopant. Above 100 K, there appears to be another activation energy of roughly 47 meV (≈ 1/4 Eg) before complete ionisation occurs above 150 K with a carrier concentration of ≈ 6 × 10^{17} cm^{-3}. The 47 meV level observed may be attributed to Hg vacancies in the sample not completely annihilated during the second step of the anneal. The absence of this behaviour in other samples suggest that MCT108, being slightly thicker that the other samples, may require a longer Hg vacancy removal anneal. As with MCT107, the annealed MCT108 material was observed to be compensated by the presence of electrons with a carrier concentration of 7.1 × 10^{15} cm^{-3} and a mobility of 7,600 cm^{2}/V.s at 77 K. This electron temperature dependency is also indicated in Figure 4.

A summary of 77 K carrier concentrations for 4 samples, before and after annealing (where available) are shown in Table II. The general observation is that for all samples, under the activation anneal conditions used, only about 20% of arsenic incorporated has been activated at 77 K. This implies that a more effective annealing strategy will have to be employed, either performing the anneal for a longer period or at a higher temperature. An alternative approach proposed would be to utilise two zone anneals where Hg partial pressures are manipulated to increase the number of Hg vacancies in the material for arsenic activation, analogous to a high temperature step. This form of two step anneal involves the sample and Hg being...
placed at different temperatures (2 separate zones) in the first step followed by the standard 240 °C anneal for 24 hours. This has the added advantage of requiring lower annealing temperatures, preserving the integrity of the sample and preventing any inter-diffusion processes from occurring when used in a grown p-n junction.

CONCLUSION

In this work, several MBE grown HgCdTe layers doped with arsenic utilising a cracker cell were successfully characterized via techniques which included FTIR, SIMS, Hall and QMSA. The incorporation dependencies of arsenic as functions of growth temperatures and arsenic cell temperatures were investigated. The results show that lower bulk cell and higher cracker cell temperatures could be used to achieve a particular doping level, reducing the amount of arsenic present and hence, background impurities in the chamber. Highly doped as-grown material demonstrated n-type conduction with low carrier concentrations implying that the majority of arsenic incorporate as neutral complexes during growth. After a high temperature anneal, only about 20% of arsenic becomes activated indicating a different annealing approach is required for full activation to p-type.

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REFERENCES


