

Amphoteric behavior of arsenic in HgCdTe

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The properties of arsenic in HgCdTe are predicted using *ab initio* calculations and a statistical theory. Predictions on the amphoteric nature of arsenic are in good agreement with experimental results on material growth both by liquid phase epitaxy and molecular beam epitaxy (MBE). The experimentally observed dependence of the arsenic diffusion on mercury partial pressure is also explained by our results. A microscopic model for activating the arsenic as an acceptor is suggested, and requirements of post-MBE-growth activation anneals are identified. © 1999 American Institute of Physics. [S0003-6951(99)00705-6]

Hg_{1-x}Cd_xTe is the material system of choice for high-performance sensing in the long-wave infrared (LWIR). A *p*-on-*n* heterojunction device¹ is currently the preferred device design, in which a wider gap *p*-type cap layer is grown on an LWIR *n*-type base layer with $x=0.22$, with the cap layer doping usually >100 times higher than the base layer doping. Although doping of the base layer with $\sim 10^{15}$ cm⁻³ indium is well in hand, the cap layer doping is more complex. The group V elements have been identified as the most desirable *p*-type dopants because of their low diffusion coefficients, compared with the native acceptor and the group I elements in HgCdTe. Liquid phase epitaxial (LPE) growth results in amphoteric incorporation of the group V elements,² with *n*-type behavior resulting when grown from the tellurium-rich melt, therefore necessitating growth from the mercury-rich melt, with its accompanying high pressures, to obtain *p*-type behavior.³ Although molecular beam epitaxy (MBE) is done at much lower temperatures than LPE, and thus offers some distinct advantages, the group V impurities are observed to incorporate as donors. Post-growth “activation” anneals at higher temperature are currently used to render the cap layer *p* type.⁴⁻⁶ If activation anneals are performed at temperatures much above the growth temperature, the advantages of the low growth temperature of MBE are reduced. Although models of the amphoteric behavior have been suggested,^{7,8} there has been no general consensus on the microscopic mechanism of group V element incorporation both in LPE and MBE material. Arsenic is the group V element that has received the most attention in the past few years, and for that reason, we focus our attention on it.

In this letter, we present the results of a theoretical examination of the behavior of arsenic atoms in Hg_{1-x}Cd_xTe. Our focus is on the thermodynamic conditions relevant to LPE growth, the dependence of arsenic diffusion on the mercury partial pressure, equilibrium conditions of post-growth anneals, the quasi-equilibrium conditions that are present during MBE growth, and nonequilibrium effects of MBE.

The calculations of thermodynamic behavior of arsenic in HgCdTe can be divided into two major parts: (1) the calculation of energies of native defects and arsenic in the material, and (2) the statistical theory from which the concentrations of arsenic in the various configurations can be

predicted. Details of the calculations are similar to those reported previously^{9,10} and are only briefly summarized here. The ground and excited state energies for native point defects and arsenic in the lattice are calculated using the full potential linearized muffin-tin orbital method¹¹ within the local density approximation (LDA). Gradient corrections¹² were added to the LDA so that the vapor pressure of the mercury monomer can be used to compare with the experiment.¹³ Defect energies were calculated using supercells containing 32 lattice sites. For the native point defects, LDA calculations were done for both HgTe and CdTe hosts, and the values at intermediate compositions were determined by a linear interpolation. For arsenic on the tellurium sublattice, calculations were done with from one to four near-neighbor cadmium.

The statistical model we use is the electronic quasi-chemical formalism,⁹ with Fermi-Dirac statistics for the electronic excitations. Vibrational free energies are calculated using a valence force-field model.¹⁴ Experimental expressions for the temperature- and *x*-dependent band gap were used.¹⁵ Bounds for the existence region for Hg_{1-x}Cd_xTe have also been taken from experiment.¹⁶

Various means of arsenic incorporation were included in the analysis, as given in Table I. The native point defects included in the present analysis are also summarized in Table I. The ionization energies for arsenic on the tellurium site behaved as an acceptor and for the first acceptor level for the cation vacancy were taken from experiment. An ad hoc shift of 0.22 eV was added to the donor level of the arsenic on the cation sublattices to account for the LDA band gap error.

In Fig. 1, the calculated defect concentrations are plotted as a function of mercury partial pressure at 500 °C, a temperature typical of LPE growth. Arsenic atoms are found to reside predominantly on the anion sublattice under mercury-

TABLE I. Arsenic and native point defects included in the analysis. Notation is as follows: The primary symbol refers to the species, the subscript refers to the site that the species occupies, *V* corresponds to a vacancy, and *I* an interstitial at a tetrahedral site.

Isolated native point defects:	V_{Hg} , Te_{Hg} , and Hg_I , V_{Te} , Hg_{Hg} , and Te_I
Native defect complexes:	$\text{Te}_{\text{Hg}}-V_{\text{Hg}}$
Isolated arsenic defects:	As_{Hg} , As_{Te} , and As_I
Arsenic defect complexes:	$\text{As}_{\text{Hg}}-\text{As}_{\text{Te}}$ and $\text{As}_{\text{Hg}}-V_{\text{Hg}}$ $\text{As}_{\text{Te}}-\text{Hg}_I$ and $\text{As}_{\text{Hg}}-\text{Te}_{\text{Hg}}$

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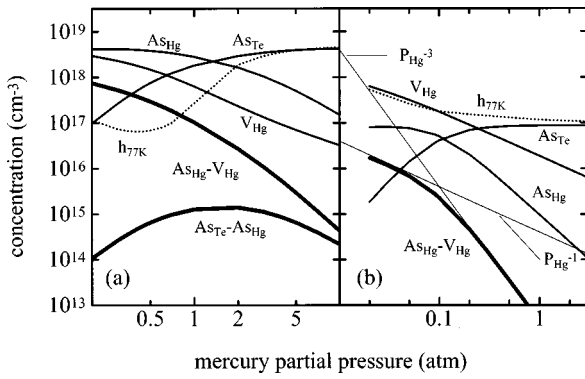


FIG. 1. Defect concentrations as a function of mercury partial pressure throughout the existence region of Hg_{0.8}Cd_{0.2}Te, for a fixed arsenic concentration of (a) 5 × 10¹⁸ cm⁻³ at 500 °C and (b) 10¹⁷ cm⁻³ at 400 °C. All concentrations represent a sum over all the charge states of the defects. The cation vacancy V_{Hg} is predicted to be a single acceptor in this range of alloy composition. Both As_{Hg}-V_{Hg} and As_{Hg}-As_{Te} are neutrals only. The dotted line is the hole concentration at 77 K assuming the high temperature defect structure is frozen in.

saturated conditions, where they behave as acceptors. Under tellurium-saturated conditions the arsenic atoms are predicted to occupy the cation sublattice predominantly, where arsenic behaves as donors, and with a large fraction of the arsenic atoms bound to cation vacancies. Under all equilibrium conditions examined, the arsenic interstitial density is negligible. This amphoteric behavior of arsenic is consistent with LPE results.^{2,3} In Table II, some of the electrical properties of LPE material are examined when they are subjected to tellurium- and mercury-saturated anneals at low temperature. Such low temperature anneals have been found to modify the vacancy concentrations, but not the electrical activity of the arsenic in the lattice,^{2,4-6} and thus no site transfer has been assumed in the theoretical results reported in Table II. Our predictions are in good agreement with experiment for the 200 °C mercury-saturated anneal. Under tellurium-saturated conditions, a large degree of compensation occurs and the exact carrier concentrations are thus very sensitive to energies we calculate for the various defects.

Next we consider the nature of arsenic diffusion. Our present and previous¹⁴ studies indicate that As_I, V_{Te}, and Te_I, by which As_{Te} might diffuse in the lattice, have extremely low densities. Our results also show that there is a significant fraction of the arsenic residing on the cation sublattice, even under cation-saturated conditions, and that there is a high concentration of cation vacancies. This suggests

TABLE II. Behavior of arsenic in LPE Hg_{0.8}Cd_{0.2}Te.

Material	77 K carrier concentrations (cm ⁻³)		
	200 °C Te-saturated	200 °C Hg-saturated	500 °C Hg-saturated / 200 °C Hg-saturated
Te-rich LPE ^a	1.4 × 10 ¹⁶ p type	1.5 × 10 ¹⁴ n type	4.4 × 10 ¹⁵ p type ^b
Theory	2 × 10 ¹⁴ n type	5 × 10 ¹⁴ n type	4.4 × 10 ¹⁵ p type
Te-rich LPE ^a	2.1 × 10 ¹⁶ p type	6 × 10 ¹⁴ n type	1.2 × 10 ¹⁷ p type ^b
Theory	1.2 × 10 ¹⁵ n type	2 × 10 ¹⁵ n type	1.2 × 10 ¹⁷ p type
Hg-rich LPE		10 ¹⁸ p type	10 ¹⁸ p type
Theory		10 ¹⁸ p type	10 ¹⁸ p type

^aTaken from Ref. 2.

^bThe arsenic concentration in the calculations were chosen to match this value.

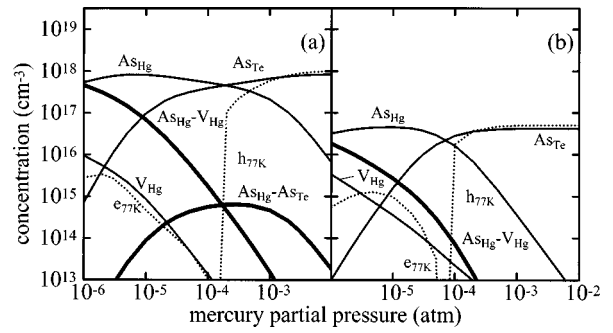


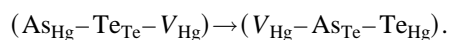
FIG. 2. Defect concentrations as a function of mercury partial pressure throughout the existence region of Hg_{0.7}Cd_{0.3}Te at 185 °C, for a fixed arsenic concentration of (a) 10¹⁸ cm⁻³ and (b) 5 × 10¹⁶ cm⁻³. All concentrations represent a sum over all the charge states of the defects. The dotted line is the hole concentration at 77 K assuming that the defect structure at the growth temperature is frozen in.

that arsenic diffusion might occur via the As_{Hg}, mediated by the V_{Hg}. If so, the arsenic diffusion will be proportional to the concentration of As_{Hg}-V_{Hg}. The pressure dependence of the As_{Hg}-V_{Hg} complex is indicated in Fig. 1 for a temperature of 400 °C and a total arsenic concentration of 10¹⁷ cm⁻³. At low mercury partial pressures, we predict the arsenic diffusion will be proportional to P_{Hg}⁻¹, while at higher mercury partial pressures, we predict the arsenic diffusion will be proportional to P_{Hg}⁻³. This is in good agreement with the experimental results of Chandra *et al.*¹⁷ who find a similar pressure dependence for a comparable temperature and arsenic concentration. Our results are also supported by experimental findings¹⁸ that arsenic diffusion at T < 300 °C under Hg-saturated conditions result in n-type material, indicating that arsenic diffuses as a donor and may not equilibrate by transferring to the anion sublattice at low temperatures, even under mercury-saturated conditions.

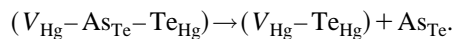
We now turn our attention to the behavior of arsenic in Hg_{0.7}Cd_{0.3}Te grown by MBE. High quality MBE growth is restricted to a very narrow growth window, both in mercury flux and temperature, and because of the high vapor mercury pressures over the solid, is restricted to the tellurium-saturated edge of the existence region.¹⁹ In Fig. 2, the defect concentrations are plotted as a function of the mercury partial pressure at 185 °C, a temperature typical of MBE growth. The left edges of Figs. 2(a) and 2(b) represents the tellurium-saturated conditions present during MBE growth. Also shown in Fig. 2 are the carrier concentrations at 77 K if the defects at 185 °C are frozen in. We find n_{77 K} ≈ 3 × 10¹⁵ cm⁻³ and n_{77 K} ≈ 10¹⁵ cm⁻³ for arsenic concentrations of 10¹⁸ cm⁻³ and 5 × 10¹⁶ cm⁻³, respectively, in rough agreement with experimental values⁶ of n_{77 K} ≈ 8.2 × 10¹⁴ cm⁻³ and n_{77 K} ≈ 6.7 × 10¹⁴ cm⁻³. If the material prepared under MBE conditions is subjected to a mercury-saturated anneal at 250 °C, carrier concentrations of n_{77 K} ≈ 2.4 × 10¹⁵ cm⁻³ and n_{77 K} ≈ 6.9 × 10¹⁴ cm⁻³ are found experimentally for the aforementioned arsenic concentrations.⁶ Our theory predicts n_{77 K} ≈ 5 × 10¹⁶ cm⁻³ and n_{77 K} ≈ 2 × 10¹⁵ cm⁻³ for these arsenic concentrations if arsenic is not permitted to change sublattices, but only the vacancy concentrations requilibrate. Thus, our calculations explain the behavior of arsenic in MBE material assuming quasi-equilibrium conditions prevail, with no need to resort

to nonequilibrium aspects of MBE. Even though the arsenic dimer and tetramer are strongly bound in the vapor phase, we do not predict complexes containing multiple arsenic atoms are present in the MBE material, nor are such complexes necessary to explain the experimental findings.

The question now arises as to how to obtain *p*-type doping with arsenic in MBE. There has been success in obtaining acceptor behavior in arsenic-doped MBE-grown material using post-growth high temperature anneals,⁴⁻⁶ but the need to resort to such high temperatures negates much of the advantage of the low growth temperature of MBE. We recently proposed a mechanism for transfer of the arsenic from the cation to anion sublattice (the essential step in the activation process).¹⁰ The starting defect for the transfer is the arsenic on a cation site bound to a mercury vacancy, $As_{Hg}-V_{Hg}$, with a tellurium on the intervening anion sublattice, Te_{Te} . From Fig. 2, we see that this defect complex will be present in large densities in as-grown MBE material. In the first step of the activation process, the intervening tellurium will transfer into the cation vacancy site, creating a tellurium antisite, with the arsenic following and transferring to the vacated tellurium site and leaving behind a cation vacancy:



In the final step, the neutral cation vacancy-tellurium antisite pair, which was previously shown to form a bound pair,²⁰ will diffuse away from the arsenic atom, which now resides on the tellurium sublattice and behaves as an acceptor,



A product of the transfer process will be the $V_{Hg}-Te_{Hg}$ complex, whose density will be supersaturated and which must diffuse to an atom sink such as a surface for annihilation.

This activation model suggests that cation vacancies effectively catalyzed the site transfer (they are present both prior to and following the site transfer). Thus an effective activation annealing strategy must preserve the cation vacancies until the site transfer of the arsenic atoms from the cation to the anion sublattice is complete. Our model explains the apparent failure of the 250 °C mercury-saturated anneal in affecting the site transfer: Even though in equilibrium arsenic should reside on the anion sublattice under these annealing conditions, the majority of the mercury vacancies are annihilated under these low temperature, mercury-saturated conditions before the site transfer can take place, and thus equilibrium of arsenic will take much longer than the 24 h typically employed for such anneals. We predict that activation can take place under mercury-saturated conditions if high temperatures are used so that there is a relatively high vacancy concentration¹⁴ or at low temperatures if the phase field from tellurium- to mercury-saturated conditions is traversed slowly.

The theoretical results presented in this letter explain the microscopic mechanism for the amphoteric behavior of arsenic in both LPE- and MBE-grown material and in subsequent processing, in terms of equilibrium thermodynamics. The results unambiguously indicate that arsenic atoms residing on the cation sublattice account for the donor-like incorporation under tellurium-saturated conditions, and that arsenic interstitials do not account for a significant fraction of

the incorporation. We suggest that low temperature anneals may be used to activate the arsenic in MBE material if the phase field from tellurium- to mercury-saturated conditions is traversed slowly. It may be possible to encourage incorporation of arsenic atoms directly on the anion sublattice by growing on the (111)A or (211)A surfaces, which are cation rich and therefore present mostly anion sites to the incoming flux, although thermodynamics will still not favor incorporation of arsenic as an acceptor under MBE conditions. Unfortunately, growth on the A surfaces have thus far resulted in poor quality material and exceedingly high mercury consumption,¹⁹ compared with the currently preferred (211)B.

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