

## Annealing conditions for intrinsic CdTe

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(Received 2 November 1998; accepted for publication 17 November 1998)

Equilibrium native defect densities in CdTe are calculated from *ab initio* methods, and compared with experimental results. We find that CdTe is highly compensated *p* type under tellurium-saturated conditions, with the cadmium vacancy as the dominant acceptor and the tellurium antisite as the compensating donor. This finding is in agreement with recent experiments that find a much larger deviation from stoichiometry than would be predicted by the electrically active defects. Under cadmium-saturated conditions, cadmium interstitials are predicted to dominate and the material is found to be *n* type. Native defect concentrations and the corresponding carrier concentrations are predicted as a function of processing conditions, and can serve as a guide to postgrowth anneals to manipulate the conductivity of undoped material for applications in *x*- and  $\gamma$ -ray spectrometers. Furthermore, we show that by choosing appropriate annealing conditions and extrinsic dopants, one can increase the operating efficiency of nuclear spectrometers by reducing the density of specific native defects that produce midgap trapping states. © 1999 American Institute of Physics. [S0003-6951(99)01304-2]

There has been a renewed interest in CdTe and related alloys in recent years for applications in *x*- and  $\gamma$ -ray spectrometers.<sup>1</sup> CdTe alloyed with small concentrations of ZnTe is also used as a lattice-matched substrate for HgCdTe-based infrared detectors. For both of these applications, some form of Bridgman growth is typically used.<sup>2</sup> Following growth, the material is often subjected to anneals under controlled temperature and partial pressures to getter impurities and to reduce native defects introduced during the growth at high temperatures.<sup>3</sup>

For *x*- and  $\gamma$ -ray spectrometers, highly intrinsic material is required. Although high-pressure Bridgman (HPB) growth produces the material with the highest resistivity, large single crystals are difficult to produce, and material inhomogeneities remain. While more conventional Bridgman (CB) growth results in lower resistivity material, if postgrowth annealing can be employed to reduce the native defect concentrations, resistivities comparable to or in excess of those obtained in the HPB material may be possible. The question remains as to how to select these annealing conditions so as to optimize the desired materials properties.

In this letter we calculate the equilibrium native defect concentrations in CdTe as a function of cadmium partial pressure and temperature. The calculation can be divided into two major parts: (1) the calculation of energies of native defects in the material, and (2) the statistical theory from which the concentrations of the defects can be predicted. Details of the calculations are similar to those reported elsewhere<sup>4-6</sup> and are only briefly summarized here. The ground- and excited-state energies for native point defects were calculated using the full potential linearized muffin-tin orbital method<sup>7</sup> within the local density approximation (LDA). Gradient corrections (GC)<sup>8</sup> were added to the LDA so that the vapor pressure of the cadmium monomer could be used to compare with experiment.<sup>9</sup> Defect energies were cal-

culated using supercells containing 32 lattice sites, with each supercell containing one defect, and allowing relaxation of the lattice constant and up to the second neighbor shell about the defect. Fourteen *k* points in the irreducible Brillouin zone were used, and the basis was selected so as to give an error of less than 0.005 eV per defect. The statistical model used in the electronic quasichemical formalism (EQC),<sup>4</sup> with Fermi–Dirac statistics for the electronic excitations. Defect clusters containing two primitive units cells were used in the EQC calculations. Temperature-dependent vibrational free energies were calculated using a valence force-field model and point Coulombic interaction<sup>5</sup> and were included in the defect free energies. Experimental expressions for the effective masses and temperature-dependent band gap were used.<sup>10</sup> Bounds for the existence region for CdTe have also been taken from experiment.<sup>11</sup>

The native defects included in the present analysis are summarized in Table I. In Fig. 1 the equilibrium native de-

TABLE I. Native point defects included in the analysis. Cluster energies are the energy of a four-lattice-site-size cluster containing the noted defect, and referenced to the free-atoms state. Energies include the LDA+GC, plus correction.<sup>a</sup> The vibrational free energies are not included in the energies shown here. 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. The energy of the cadmium antisite was very large, and was dropped from the analysis. The two energies for the cadmium interstitial correspond to the two tetrahedral interstitial sites. The donor and acceptor energies are given with respect to the conduction- and valence-band edges, respectively.

Defect	Cluster energy (eV)	Ionization energy (eV)
CdTe	-8.84	Neutral
$V_{\text{Cd}}$	-5.40	$a1=0.2, a2=0.8$
$\text{Te}_{\text{Cd}}$	-7.10	$d1=0, d2=0.4$
$\text{Te}_T$	-7.35	Donor
$\text{Te}_{\text{Cd}}-V_{\text{Cd}}$	-5.35	Neutral
$V_{\text{Te}}$	-3.28	$d1=0.4, d2=0.5$
$\text{Cd}_T$	-8.08, -7.75	$d1=0, d2=0.2$

<sup>a</sup>See Ref. 9.

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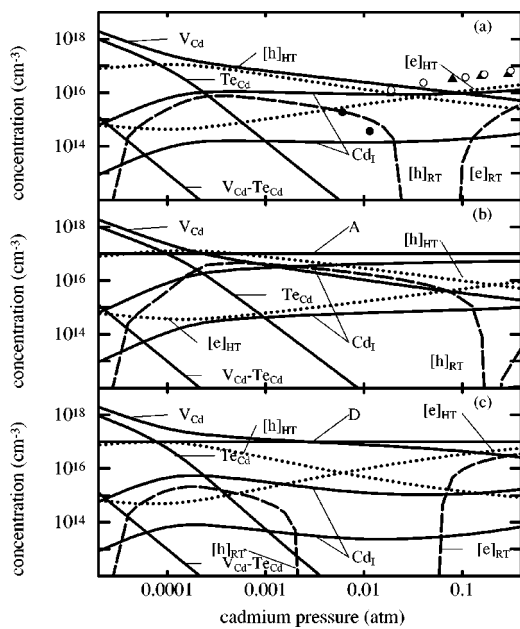


FIG. 1. Defect and free-carrier concentrations as a function of cadmium partial pressure throughout the existence region of CdTe at 700 °C for (a) undoped material and CdTe doped with (b) 10<sup>17</sup> cm<sup>-3</sup> shallow acceptor (A) and (c) 10<sup>17</sup> cm<sup>-3</sup> shallow donor (D). All concentrations represent a sum over all the ionization states of the defects. The room-temperature (RT) carrier concentrations are also shown. Also shown are high-temperature carrier concentrations from Smith (see Ref. 13) (×) and Chern *et al.* (see Ref. 12) (triangles), and room-temperature electron (open circles) and hole (filled circles) concentrations from de Nobel (see Ref. 14).

fect concentrations as a function of cadmium partial pressure are plotted for 700 °C and compared with several experimental results.<sup>12–14</sup> For the lower cadmium partial pressure regime, the cadmium vacancy is predicted to be the dominant native defect, and nearly 100% doubly ionized. The concentration of doubly ionized tellurium antisites is also quite high under tellurium-saturated conditions, resulting in a large degree of compensation. Under cadmium-saturated conditions (the higher cadmium partial pressure regime), the cadmium interstitial dominates, resulting in *n*-type material. The identity of the donor defect in cadmium-saturated material was previously unresolved in the literature; our calculations clearly indicate that the cadmium interstitial density is much higher than the tellurium vacancy density, and is the source of the *n*-type behavior.

Assuming that the native defects are frozen-in from the high-temperature equilibration conditions upon quenching to room temperature (RT), the RT carrier concentrations can be calculated by allowing just the Fermi level to reequilibrate at the lower temperature. The results of such a calculation are shown in Fig. 1. We see that the material is predicted to be intrinsic at room temperature near to the cadmium-saturated edge of the existence region. The cadmium partial pressure at which intrinsic behavior occurs is in general agreement with early experiments by de Nobel,<sup>14</sup> although our results indicate a wider range of intrinsic behavior. Significant compensation of the cadmium vacancy acceptors under tellurium-saturated conditions at 700 °C when quenched to RT is also predicted.

The regions in the pressure–temperature existence region that correspond to near-intrinsic conditions at room temperature are indicated in Fig. 2. The intrinsic regions re-

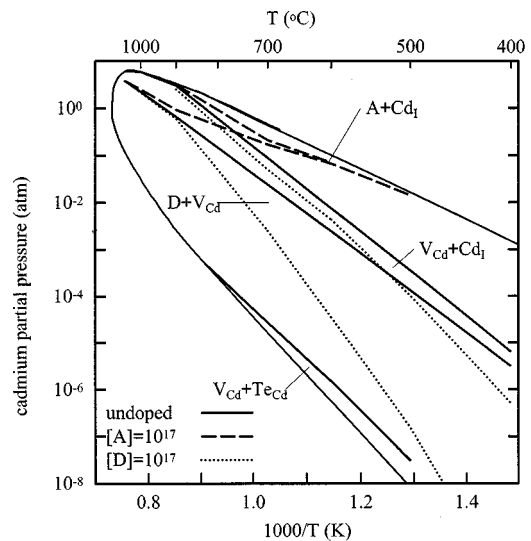


FIG. 2. Regions in the existence region of CdTe that correspond to near-intrinsic conditions (carrier concentrations less than 10<sup>7</sup> cm<sup>-3</sup>) at room temperature for both undoped material and for CdTe doped with 10<sup>17</sup> cm<sup>-3</sup> acceptors (A) or donors (D). The defect concentrations at the indicated temperature and pressure are assumed to be frozen-in upon quenching to room temperature. The dominant defects in the indicated intrinsic regions are also indicated.

sult from compensation of oppositely charged native point defects, and although the intrinsic band extends from high to low temperatures, the total number of defects is higher in the intrinsic bands at the higher temperatures. The intrinsic band along the tellurium-saturated edge of the existence region results from compensations of cadmium vacancies by tellurium antisites, while the intrinsic band nearer to the middle of the existence region results from compensations of cadmium vacancies by cadmium interstitials. The HPB material currently favored for spectrometers based on CdZnTe is likely to be intrinsic through self-compensation by high concentrations of native defects introduced at the high growth temperatures. By annealing within an intrinsic band at lower temperatures, it is possible to achieve intrinsic material with fewer compensated native defects, and by choosing the low-pressure or midpressure intrinsic band it is possible to selectively reduce the cadmium interstitial density or tellurium antisite density, respectively.

By introducing extrinsic shallow dopants to CdTe, it is possible to further manipulate the density of selected native defect populations. In Fig. 1 we have plotted the defect concentrations in CdTe for material doped with 10<sup>17</sup> cm<sup>-3</sup> shallow acceptors and donors. The RT intrinsic band near to the tellurium-saturated side of the existence region is unaffected by the presence of 10<sup>17</sup> cm<sup>-3</sup> shallow acceptors or donors. The higher pressure region corresponding to room-temperature intrinsic behavior shifts to higher (lower) cadmium partial pressures at the lower temperatures with the addition of shallow acceptors (donors).

The room-temperature intrinsic bands for doped material quenched from high temperature are shown in Fig. 2. Although the dominant intrinsic band still corresponds to compensation of cadmium vacancies by cadmium interstitials at the higher temperatures, at the lower temperatures the intrinsic behavior results from compensation of cadmium interstitials by shallow acceptors when doping with an acceptor and

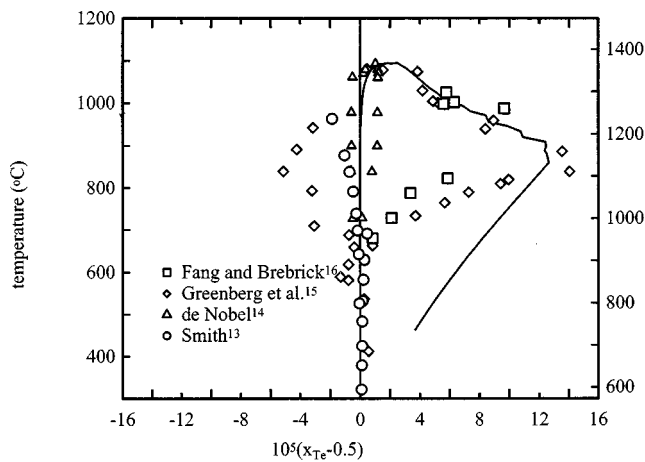


FIG. 3. Tellurium atom fraction in CdTe for cadmium- and tellurium-saturated conditions.

from compensation of cadmium vacancies by shallow donors in the case of donor doping.

Although the atomic fractions of cadmium and tellurium in CdTe are nominally 0.5, native point defects in the material cause small deviations from this value. Based on our predicted native defect concentrations, the tellurium atomic fraction has been calculated as a function of temperature for tellurium- and cadmium-saturated conditions; results are shown in Fig. 3. We note that the deviations from stoichiometry are in good agreement with recent experiments on tellurium-saturated material,<sup>15,16</sup> which show nearly an order of magnitude larger deviation from stoichiometry than earlier results based on electrical measurements.<sup>13,14</sup> The large deviation from stoichiometry arises from cadmium vacancies and tellurium antisites, which produce highly compensated *p*-type material.

Given the dominance of cadmium vacancies under tellurium-saturated conditions and of cadmium interstitials under cadmium-saturated conditions, if the diffusivities of the cadmium vacancies and interstitials are comparable, the cation diffusion mechanism is likely to be dominated by these two defects in the two different extremes of the existence region, with  $D \propto [V_{Cd}]$  at low cadmium partial pressures, and  $D \propto [Cd_i]$  at high cadmium partial pressures.<sup>17</sup> Such a dependence is indicated by recent diffusion measurements using manganese marker layers,<sup>18</sup> although earlier experiments at high temperatures found *D* to be independent of the cadmium partial pressure.<sup>19–21</sup> Based on the results of our calculations, the interpretations in Ref. 18 for diffusion under cadmium-saturated conditions that relies on diffusion via tellurium vacancies, and requires the formation of a cation antisite, is highly unlikely.

From our results, we expect that the HPB material currently favored for spectrometers based on CdZnTe is likely to be intrinsic through self-compensation by native defects introduced at the high growth temperatures. Although intrinsic material at RT can be achieved by annealing at a variety of temperatures, anneals at lower temperatures will, in general, reduce the total density of native defects. Thus, by sub-

jecting material prepared by either HPB or CB techniques to anneals at temperatures lower than the growth temperature with a controlled cadmium partial pressure, it should be possible to reduce the self-compensating defect densities, and still produce intrinsic material. Furthermore, by designing proper anneals for material into which a controlled density of extrinsic shallow dopants have been introduced, the density of individual native defects, which have been identified at harmful traps, can be reduced below those achievable in intrinsically self-compensated material. Preanneals may be needed to remove tellurium precipitates resulting from the retrograde solubility of tellurium, so that anneals can be performed off of the tellurium-saturated side of the existence region. Extension of these calculations to CdTe-based alloys is straightforward.

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<sup>9</sup>Although the addition of the gradient corrections to the LDA improves the prediction of the cohesive energy compared with the straight LDA results, in CdTe the LDA+GC calculations predict an underbinding of the compounds by  $\sim 0.04$  eV per bond. We have corrected this discrepancy with experiment by shifting the free-atom energies of the cation and anion atoms by an equal amount so as to result in the proper experimental binding energy.

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