Hydrogen Transport Vapor Phase Epitaxy of CdTe on Hybrid Substrates for X-Ray Detector Applications

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The growth of thick CdTe epitaxial layers by the hydrogen transport vapor phase epitaxy (H_2T-VPE) method is reported for the first time. The thermodynamics of the H_2 transport method of CdTe is analyzed to determine the equilibrium partial pressures of the molecular species in the vapor and its supersaturation as a function of growth conditions. (100)-oriented CdTe epilayers are successfully grown by H_2T-VPE on hybrid ZnTe/GaAs(100) substrates prepared by metalorganic vapor phase epitaxy. Growth rates up to 10 μm/h are obtained at temperatures ~760°C and with the CdTe source temperature at 827°C. The achievement of even higher growth rates can be foreseen by using the present method under slightly different conditions; several hundreds micron thick CdTe layers can be thus grown by the H_2T-VPE. CdTe samples have mirror-like, nearly featureless surfaces. Also, CdTe epilayers have shown a medium-to-high resistivity at room temperature, possibly as a result of compensation by donor impurities diffusing from GaAs. Still the growth of highly resistive layers by *in-situ* chlorine doping during the H_2T-VPE growth is possible. In summary, H_2T-VPE is a potential alternative to traditional melt- and vapor-growth methods for the synthesis of detector-grade CdTe for application to the 1–100 keV x-ray energy range.

Key words: CdTe, H_2T-VPE growth, x-ray detector applications

INTRODUCTION

CdTe-based detector performances are presently limited by charge collection distortion and noise effects, both due to the poor quality of CdTe crystals.[1] Bulk crystals suffer from large inhomogeneities of both their crystalline and electrical properties. Although highly resistive CdTe:Cl (with resistivity >10^6 Ω·cm) can be achieved, the growth of detector-grade CdTe crystals remains rather unreproducible due to difficulties in controlling the compensation of native defects (namely, Cd vacancies) during quasi-equilibrium melt-growth methods. Furthermore, the diameter of CdTe crystals achieved by these methods is limited to about 1–1.5″ by severe structural problems. Vapor crystallization has advantages over melt-growth: i.e., lower growth temperatures (which reduce point defect concentrations) and higher material purity. Although such advantages are common to both bulk and epitaxial growth methods, most of the efforts have been traditionally directed toward bulk growth, as nuclear detectors for x- and γ-ray photons with energies well above 100 keV require several mm of CdTe,[2] which can only be obtained by bulk growth. However, x-ray photon detection in the 1–100 keV energy range (for both medical applications and astrophysics research) requires much smaller sensitive volumes, corresponding to less then 500 μm.[2] This brings the growth of detector-grade CdTe within the limits of a vapor phase epitaxy (VPE) method, despite the fact that established VPE technologies have low growth rates and high process costs. Still, the use of open VPE methods for CdTe would make stoichiometry control much easier than in closed systems, so as for intentional doping. Also, VPE methods would have the additional advantage over traditional bulk growth of allowing CdTe deposition on large areas (>2″ dia. wafers) with a high lateral homogeneity.

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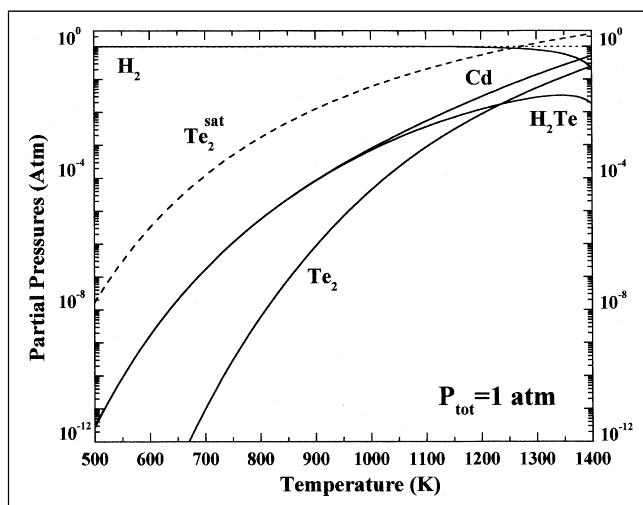


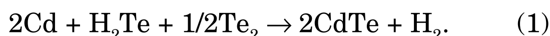
Fig. 1. Partial pressures of the vapor phase molecular species H_2, Cd, Te_2 and H_2Te in equilibrium with solid CdTe as a function of temperature. P = 1 atm is the total pressure of the vapor phase.

Finally, the growth of detector-grade epitaxial CdTe would allow a much easier integration of the device with the usual Si-based electronics.

A suitable VPE technology for the production of detector-grade CdTe should thus allow the growth of thick (up to 500 μm) highly resistive CdTe epilayers and at fairly low cost. High CdTe growth rates are a necessary requirement for such a method. In this work we report for the first time on the use of the H_2 transport vapor phase epitaxy (H_2T-VPE) method for the growth of relatively thick (100)-oriented CdTe epitaxial layers on hybrid substrates. A thermodynamic analysis of this method is presented along with early data of CdTe growth and characterization. Present results show the potentials of the H_2T-VPE as a low cost method for the growth of detector-grade epitaxial CdTe for applications to the 1–100 keV x-ray photon detection.

BASICS OF H_2T-VPE AND THERMODYNAMICS

The H_2T-VPE method is based on the high temperature H_2 reduction of a solid CdTe phase to produce Cd, H_2Te and Te_2 vapor species, according to the well-known reactions:[3] i) $CdTe + H_2 \rightarrow Cd + H_2Te$ and ii) $H_2Te \rightarrow H_2 + 1/2Te_2$. The gas mixture formed is then transported at atmospheric pressure by the H_2 flow to a lower temperature deposition region for the epitaxial growth of CdTe, according to the overall VPE reaction:



$$2Cd + H_2Te + 1/2Te_2 \rightarrow 2CdTe + H_2. \quad (1)$$

To determine the vapor phase composition during the H_2T-VPE process of CdTe, we have performed a thermodynamic calculation of the species vapor pressures in equilibrium with the solid, assuming perfect stoichiometry (i.e., Cd:Te = 1:1) for the CdTe solid phase. Figure 1 shows the result of these calculations for a total vapor pressure P = 1 atm. It appears that the H_2 reduction of CdTe leads to the production of Cd, Te_2 and H_2Te molecules in the vapor, whose equilibrium pressures increase with temperature. It appears that the volatile H_2Te molecule predominates over Te_2 at low temperatures, the latter being the most abundant Te-containing species only above ~1200K. Still, the Te_2 partial pressure stays always below its saturated vapor pressure value (the dashed curve in Fig. 1), above which a solid Te phase precipitates. More details on these calculations will be reported elsewhere.

The results of Fig. 1 were used to calculate the vapor phase supersaturation of the H_2T-VPE process of CdTe as a function of both source (T_S) and deposition (T_D) temperatures. On the basis of the overall reaction in Eq. (1) above, the supersaturation turns out to be

$$\frac{\Delta\mu}{RT_D} = \ln\left[\frac{\left(\frac{p_{Cd}}{p_{Cd}^{eq}}\right)\left(\frac{p_{Te_2}}{p_{Te_2}^{eq}}\right)^{1/4}\left(\frac{p_{H_2Te}}{p_{H_2Te}^{eq}}\right)^{1/2}}{\left(\frac{p_{H_2}}{p_{H_2}^{eq}}\right)^{1/2}}\right], \quad (2)$$

where $\Delta\mu = \mu_{vap}(T_S)-\mu_{cryst}(T_D)$ is the chemical potential difference between the reactant vapor mixture (assumed as the equilibrium chemical potential of the mixture at the source temperature) and the growing CdTe crystal. Values of $\Delta\mu/RT_D$, ranging between zero (for $T_D = T_S$) and ~27÷35 (for T_D = 550K), are reported in the inset of Fig. 2 as a function of the growth temperature and for three different source temperatures. Moreover, $\Delta\mu/RT_D$ increases by either lowering T_D or increasing the source temperature, as expected for an esothermic growth process. Figure 2 shows the values of the thermodynamic function [1-exp(-$\Delta\mu/RT_D$)], which is expected to modulate the forward kinetic rate of Eq. (1) and thus the effective CdTe

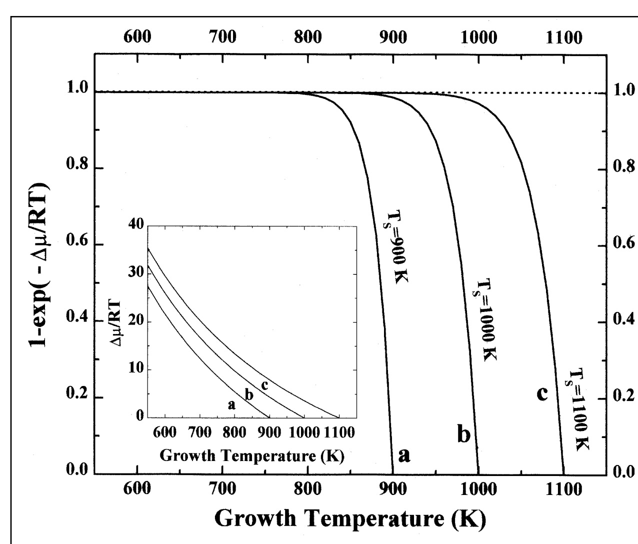


Fig. 2. Calculated values of the thermodynamic function [1-exp(-$\Delta\mu/RT_D$)] and of the vapor phase supersaturation $\Delta\mu/RT_D$ (inset) as a function of the CdTe growth temperature T_D and for three different source temperatures T_S, namely, (a) 900, (b) 1000, and (c) 1100K.

growth rate.[4] Figure 2 shows that a rapid drop of the growth rates is expected for substrate temperatures approaching the source value, as the thermodynamic driving force of the process dies off. On the contrary, at sufficiently lower growth temperatures the process will only be limited by the kinetics of CdTe growth reactions. This will be discussed later on.

EXPERIMENTAL

Nominally undoped CdTe epitaxial layers were grown by the H_2T-VPE method using a purposely designed epitaxial reactor. In order to induce the (100) nucleation of CdTe, all depositions were performed on ZnTe/GaAs(100) hybrid substrates,[5] the latters grown by metalorganic vapor phase epitaxy (MOVPE). The ZnTe buffer layers were deposited on

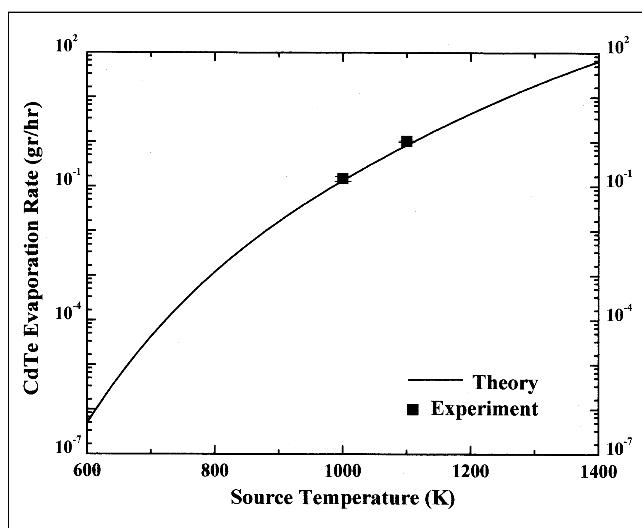


Fig. 3. Experimental (solid squares) and calculated values of CdTe source evaporation rate as a function of the source temperature.

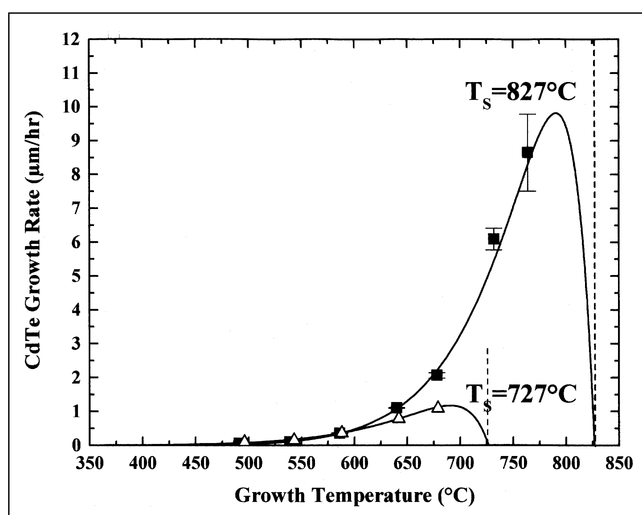


Fig. 4. CdTe epilayer growth rates as a function of the substrate temperature. The two sets of data points refer to two different source temperatures T_S, i.e. 727 (a) and 827°C (b). The solid lines represent calculated values obtained from the semi-empirical growth rate expression $A \cdot \exp(-E_A/RT_D) \cdot [1-\exp(-\Delta\mu/RT_D)]$, with E_A taken as: (a) 22.9 kcal/mol and (b) 32.8 kcal/mol.

S.I. (100)GaAs substrates at 350°C in an Aixtron model 200RD MOVPE reactor, using electronic grade dimethyl-zinc and di-isopropyl-telluride as zinc and tellurium precursors, respectively.[6] The procedures for the preparation of the GaAs substrates immediately before the MOVPE growth are also reported in Ref. 6. ZnTe epilayers ~0.4 μm thick were used for improved crystallinity of the overgrown CdTe epilayers.[5] After unloading from the MOVPE chamber, the ZnTe/GaAs samples were kept into a dry-box connected to the MOVPE reactor to avoid oxidation of the ZnTe surface; the samples were then directly loaded into the H_2T-VPE chamber immediately before CdTe depositions, without any *ex-situ* surface treatment. Cubic polycrystalline 5N pure CdTe powder (from Cerac, Inc.) was used as source material in the H_2T-VPE reactor and reduced at high temperature under pure H_2 flow for 1 h immediately before the growth started. Typical H_2 flow rates ranged around 1.0 l/min. H_2T-VPE growth temperatures were varied in the 580°C–810°C interval, the source material being kept at either 727 or 827°C. CdTe growth times ranged between 30 min and a few hours. After the growth, the samples were cooled down to room temperature under a 6.0 N pure N_2 flow.

Single crystal x-ray diffraction (XRD) θ-2θ measurements were performed routinely on the samples to check for the epitaxy of as-grown CdTe/ZnTe/GaAs heterostructures. The surface morphology of the as-grown samples was investigated by scanning electron micrographs (SEM) performed on a Philips model XL20 microscope operated at 20 kV accelerating voltage. Also, SEM observations of sample cross-sections obtained by cleavage along the ⟨110⟩ planes were used to measure the thickness of CdTe. Finally, room temperature Hall measurements were performed in the Van der Pauw configuration using ac currents and a 0.32 Tesla magnetic field. To this purpose, gold contacts were evaporated onto the CdTe samples.

RESULTS AND DISCUSSION

Growth experiments were performed by keeping the CdTe powder source either at 727 or 827°C. Figure 3 reports the experimental data of the source evaporation rates as derived by weight loss measurements of the CdTe charge. The solid line in the figure represents the theoretical estimate of the CdTe charge transport rate as a function of the source temperature and assuming perfect equilibrium between the solid CdTe and the vapor phase, according to what reported in Fig. 1. Experimental points agree with theoretical values within a 20–30% error, the latter being ascribable mostly to the precision of thermodynamical calculations.

XRD measurements have shown that (100)-oriented CdTe layers can be reproducibly grown on ZnTe/GaAs hybrid substrates. CdTe layers with thicknesses between 0.5 and 22.8 μm were obtained; these results are reported in Fig. 4 where corresponding CdTe growth rates are shown as a function of substrate temperature, for the two source temperatures

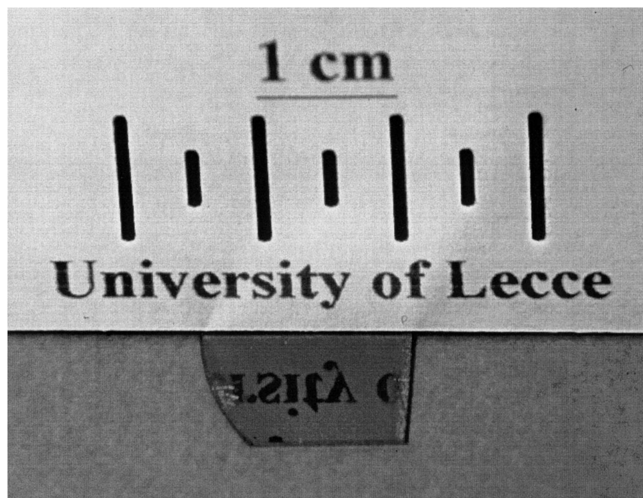


Fig. 5. Photograph of a 22.8 μm thick CdTe epilayers grown on a ZnTe/GaAs(100) hybrid substrate. The surface of CdTe appears mirror-like.

10μm

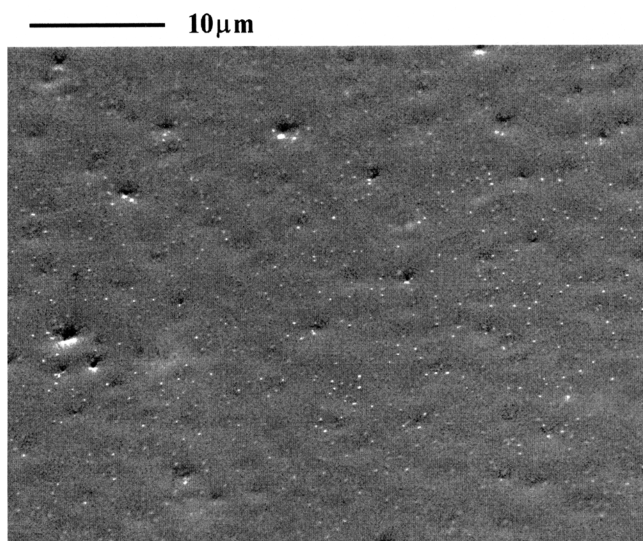


Fig. 6. Surface scanning electron micrograph of the same sample as in Fig. 5. The morphology of the CdTe layer is smooth and nearly featureless on a 10 μm scale.

above. A logarithmic plot of the growth rates as a function of inverse temperature (Arrhenius plot) has shown a distinctive linear increase, as expected for a thermally activated process. Values of the apparent activation energy E_A for the two sets of data were obtained by best fitting the low (⟨650°C) temperature growth rates with a $A \cdot \exp(-E_A/kT_D)$ function. Values of E_A turned out to be 22.9±1.5 kcal/mol and 32.8±1.1 kcal/mol for the 727 and 827°C source temperatures, respectively, indicating a growth process activated by surface reaction kinetics. The solid curves in Fig. 4 represent the expected growth rates, as calculated on the basis of the semi-empirical function $A \cdot \exp(-E_A/kT_D) \cdot [1-\exp(-\Delta\mu/RT_D)]$, taking into account both kinetics and thermodynamics. It appears that, while CdTe growth rates do not exceed 1 μm/h in the case of 727°C source temperature, nearly 10 μm/h can be achieved by growing at ~790°C and for a source temperature of 827°C. Growth rates well above 10

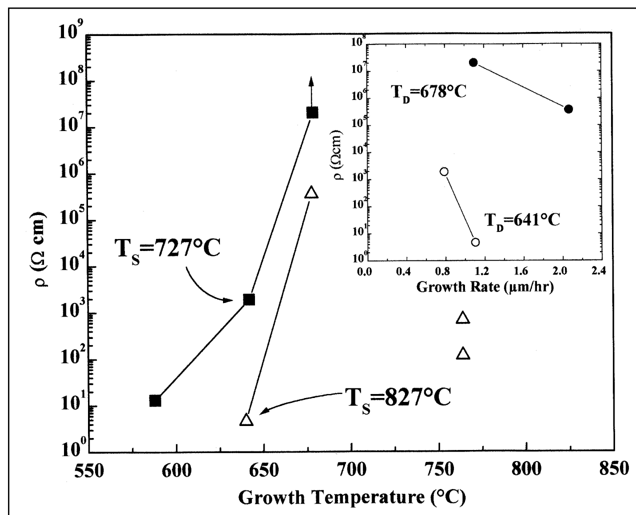


Fig. 7. Room temperature resistivities (ρ) of the CdTe epilayers as a function of their growth temperature for two different source temperatures T_S. In the figure inset ρ is reported as a function of the epilayer growth rate for two different values of the growth temperature T_D.

μm/h should be expected at higher source and substrate temperatures.

The surface appearance of the as-grown CdTe epilayers was mirror-like, as shown by the photograph in Fig. 5, which has been recorded from a 22.8 μm thick CdTe sample. Figure 6 reports a SEM micrograph obtained from the same sample, further showing that a nearly featureless morphology can be obtained by the present H_2T-VPE method.

Figure 7 reports the room temperature resistivity (ρ) as a function of sample growth conditions. It appears that ρ increases by several order of magnitude for small increases of T_D (and T_D ⟨680°C) and values of $\rho > 10^5$ Ω·cm were obtained for growth temperatures ~678°C; however, ρ also decreases by increasing the CdTe growth rate (see inset of Fig. 7). These findings can be explained by assuming that at high temperatures a donor impurity (likely Ga) diffuses from the undelying GaAs and compensates the CdTe layers. Indeed, samples grown at low temperatures and/or high growth rates have $\rho < 10^3$ Ω·cm; for these samples Hall measurements indicate values of p~3.5 × 10^{16} cm^{-3}. However, samples grown at T_D = 764°C and T_S = 827°C (growth rates ~9 μm/h) showed resistivities in the 10^2–10^3 Ω·cm range and n~ 6.7 × 10^{14} cm^{-3}, suggesting that a donor doping mechanism possibly sets in at these temperatures. Further investigations are thus required to clarify the origin of the electrical conductivity in our nominally undoped CdTe samples. Studies on the H_2T-VPE growth of CdTe:Cl epilayers are also on progress in our laboratory and will be reported elsewhere.

CONCLUSIONS

The application of the H_2T-VPE method to the growth of thick CdTe epitaxial layers was reported for the first time in this work. The thermodynamics of the H_2 transport method of CdTe was studied to determine the equilibrium partial pressures of the differ-

ent molecular species present in the vapor phase and the expected supersaturation as a function of the growth conditions. (100)-oriented CdTe epilayers were grown by H_2T-VPE on hybrid ZnTe/GaAs substrates. Growth rates close to 10 μm/h were obtained at temperatures around 760°C and with the source temperature at 827°C. Still, the achievement of even higher growth rates can be foreseen by using the present method under slightly different conditions. The as-grown CdTe samples were mirror-like in appearance, their surface being relatively smooth and featureless, as confirmed by SEM observations. Some of these CdTe samples showed a medium-to-high resistivity at room temperature, possibly as a result of compensation by donor impurities diffusing from GaAs. Still the growth of highly resistive layers could be attempted by *in-situ* chlorine doping during the H_2T-VPE growth. In summary, H_2T-VPE is a potential alternative to traditional melt- and vapor-growth methods for the synthesis of detector-grade epitaxial CdTe for application to the 1–100 keV energy range.

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