

# Epitaxial mercury cadmium telluride requirements for infrared photodiodes<sup>+</sup>

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*This paper provides primarily a short review of the methods used to grow HgCdTe with a summary of some of its basic properties and advantages and disadvantages. Methods of crystal growth of HgCdTe epitaxial layers fall generally into two classes: growth from the solution and from the vapour phase. Growth from solution has taken the form of liquid phase epitaxy (LPE) including growth from Hg-rich and Te-rich solutions and using tipping, dipping and sliding methods. In the metal organic chemical vapour deposition (MOCVD) technique, the substrate is exposed to a hot stream of gaseous compounds, and in molecular beam epitaxy (MBE) to a thermal beam of atoms and molecules. In all these methods, control of Hg pressure is a major concern. HgCdTe is the material of choice for 3–5  $\mu\text{m}$  and the 8–12  $\mu\text{m}$  wavelength IR detectors. HgCdTe is not strong or easy to work with, but the technology is maturing and sophisticated devices are now being built.*

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## 1. Introduction

The production of high resolution infrared images, limited principally in resolution by optical diffraction and in dynamic range by photon noise statistics, is the object of widespread research and development activity throughout the semiconductor industry. Progress towards this end has been made through a variety of approaches to two-dimensional closely-packed detector arrays and to the complex problem of manipulating the signals generated simultaneously by a large number of detecting elements. In recent years HgCdTe has emerged as the most strongly favoured material for detector fabrication since its energy gap (0–1.5 eV) can be tailored to match the specific needs of infrared detection and fiber optic systems [1]. The material technology has evolved from bulk grown material producing small pieces to relatively large epitaxial wafers grown in reactors with multiple wafer capability. As the overall cost becomes a greater consideration in selection of the array technology, the

quality, physical characteristics, and the cost of the material become paramount considerations in the choice of the detector technology for the imaging systems. With declining resources, these considerations must include the impact of new materials, characterisation technology, and *in situ* material growth controls on the overall performance and cost of the imaging system. As illustrated in Fig. 1, the material characteristics can play the dominant role in the selection of the sensor array configuration and in design of the imaging system [2].

The growth of high purity HgCdTe single crystals has been explored using a variety of techniques, including bulk crystal Bridgman and CRA (cast-recrystallise-anneal), and a broad spectrum of epitaxial growth techniques. Bulk HgCdTe, grown by various techniques, was used in the initial stage of detector fabrication, because of the difficulties encountered in obtaining HgCdTe epitaxial layers. However, over the two past decade maturing technology has allowed synthesis of epitaxial growth techniques currently used.

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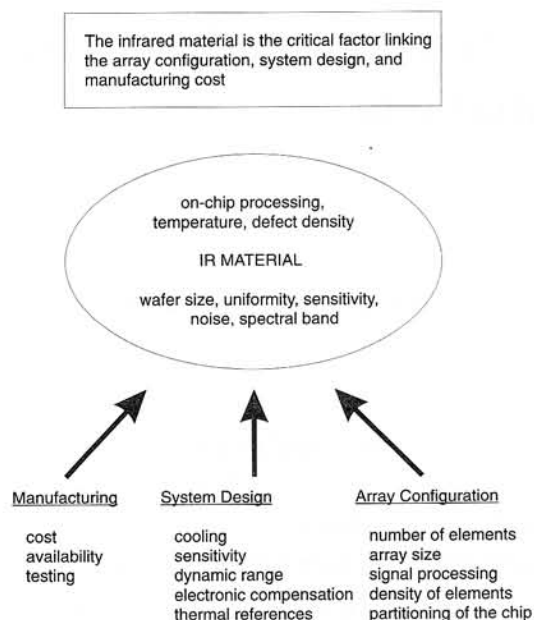


Fig. 1. The characteristics of the IR material influence both the performance and cost of the imaging system. Improvements in the properties of the material wafer can have a large impact on reducing system size and complexity (after Ref. 2).

The main difficulties that have slowed the development of epitaxial growth techniques for HgCdTe are the high Hg vapour pressure at elevated temperatures, and the large interdiffusion coefficients of Hg and Cd [3–5]. Epitaxial growth techniques have traditionally

produced higher quality material because their lower growth temperatures allow greater control of thickness, impurity background, and compositional uniformity. Lower growth temperatures have additional importance for HgCdTe as they reduce and control the Hg vapour pressure and constituent interdiffusion. Another advantage of HgCdTe for epitaxy is that near-lattice and thermal matching conditions exist over the entire compositional range, with only a 0.2% lattice mismatch between HgTe and CdTe. The epitaxial growth technology for  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  has benefited greatly from the III–V epitaxial technology base, and although its maturity lags approximately 5–10 years behind that technology, it is currently making rapid progress (Fig. 2).

## 2. Epitaxial growth techniques

HgCdTe growth is characterised by serious problems of chemistry: quite apart from the highly toxic nature of its constituents, the high partial pressure of mercury at melt temperatures may lead to explosion in sealed tube methods. As with III–V compounds, growth techniques for HgCdTe have evolved with the time. First, growth by liquid phase epitaxy (LPE) was introduced, followed by vapour phase epitaxy (VPE), and finally molecular beam epitaxy (MBE). In this section, the epitaxial techniques currently used for HgCdTe growth are discussed.

### 2.1. Liquid phase epitaxy

Liquid phase epitaxy from solutions is a convenient cost-effective growth technique for the preparation and study of thin film HgCdTe for the following reasons:

- a growth apparatus can be assembled and operated with relative ease compared with the vapour phase techniques, namely MOCVD and MBE;
- important regions of the ternary Hg–Cd–Te phase diagram have been investigated, thereby allowing estimation of melt compositions and resulting LPE film compositions for the alloy range of interest;
- the LPE growth technique is also fully compatible with major scale-up to volume production systems.

In simple terms, LPE is a solution growth technique that involves the controlled crystallization of a solute dissolved in a solvent onto a single crystal substrates as they are thermodynamically compatible and nearly lattice matched. Both Hg and Te are suitable solvents [6, 7]. The major difference between growth from Hg- and Te- rich solutions is that the Hg vapour pressure over

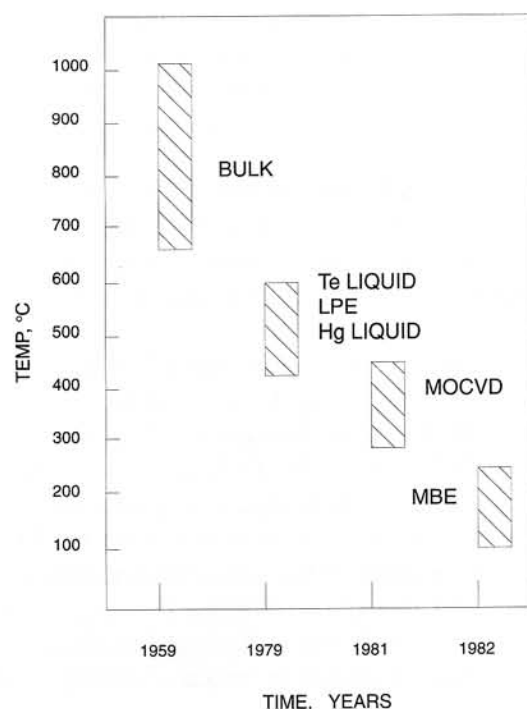


Fig. 2. Temperature ranges for growth of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  by various growth techniques versus date of first reported attempt (after Ref. 19).

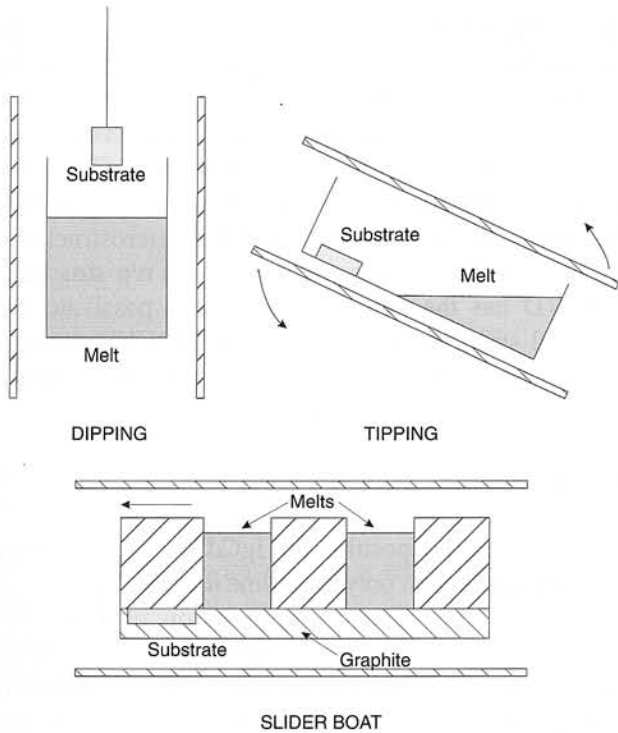


Fig. 3. Schematic illustration of dipping, slider-boat, and tipping reactors used for LPE growth (after Ref. 20).

the liquid or melt is much higher in the former case. For example, at 500°C the Hg partial pressure over Te-saturated  $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$  is 0.1 atm, while that of Hg-saturated  $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$  is 7 atm [8, 9]. Therefore, it is not surprising that many more laboratories are pursuing LPE from Te-rich melts than from Hg-rich melts. LPE layers are generally grown on (111)B CdTe or lattice-matched CdZnTe substrates in tipping, slider-boat, and dipping reactors using either Hg or Te solutions. Fig. 3 is a schematic illustration of the three basic methods of bringing the substrate into contact with the growth solution. Most LPE growth is now performed on CdZnTe substrates primarily because of improved lattice matching to the HgCdTe film and a reduced twin density compared with CdTe substrates. In addition to these factors, other beneficial aspects of CdZnTe include a lower subgrain density than for CdTe, an apparent improvement in surface morphology of the LPE film, and an increased tolerance (i.e. less terracing on the film surface) to substrate misorientation [10].

Since second-generation IR imagers based on photodiodes and photocopacitors require significantly lower carrier concentrations (low  $10^{15}$  to mid  $10^{16} \text{ cm}^{-3}$ ), controlled doping of HgCdTe is essential. A stoichiometry adjustment anneal, generally performed at temperatures ranging from 200 to 300°C in Hg-saturated atmosphere, is required to reduce the net acceptor density of as-grown films. After this anneal,

the material remains p-type or converts to n-type, depending on the nature of the residual impurities in the film. Controlled doping of HgCdTe LPE can be achieved by at least three methods:

- vacancy doping (p-type), by adjusting the stoichiometry of the material using moderate temperature (300 to 350°C) Hg-saturated annealing;
- post-growth ion implantation of a dopant followed by an anneal for dopant activation and damage removal;
- doping during LPE growth, by incorporation of impurities intentionally introduced in the growth solution.

## 2.2. Metal-Organic Chemical Vapour Deposition

Growth of epitaxial layers via vapour phase transport methods has been preferred when a high wafer handling capacity is desired. This stems from the fact that LPE growth approaches are usually difficult to scale up to handle in a single growth run the multiple wafers necessary for large output. Another important aspect of vapour phase epitaxy is that deposit and substrate need not be thermodynamically compatible, a necessary precondition for LPE growth.

As in the case of LPE, the development of VPE techniques for HgCdTe has been slowed by the high vapour pressure of Hg necessary to maintain the compositional stability of the grown layer. Thus, most vapour phase HgCdTe epitaxial growth has been carried out in closed ampoules, where the equilibrium vapour pressure of Hg can be readily controlled. Open-tube vapour phase methods for the synthesis of epitaxial HgCdTe have recently been explored, with encouraging results. MOCVD has been used successfully over the past two decades to synthesise device quality III–V layers. Concurrently, at a much smaller effort, the growth of the lower pressure II–VI compounds, i.e. CdTe, ZnSe and ZnTe, and solid solutions by MOCVD resulted in epitaxial layers. In the growth of HgCdTe by MOCVD has previously been reported [11, 12] where mercury was introduced as a liquid Hg source, together with diethyltelluride ( $\text{Et}_2\text{Te}$ ) and dimethylcadmium ( $\text{Me}_2\text{Cd}$ ). The epitaxial growth is achieved in a horizontal reactor at atmospheric pressure [12]. In this growth process, the layer constituents are transported to the reaction zone via a carrier gas (typically high purity  $\text{H}_2$ ) in the form of metal alkyls. The metal alkyls considered for this use are liquid at or near room temperature, and exhibit appreciable vapour pressure. The simplicity of

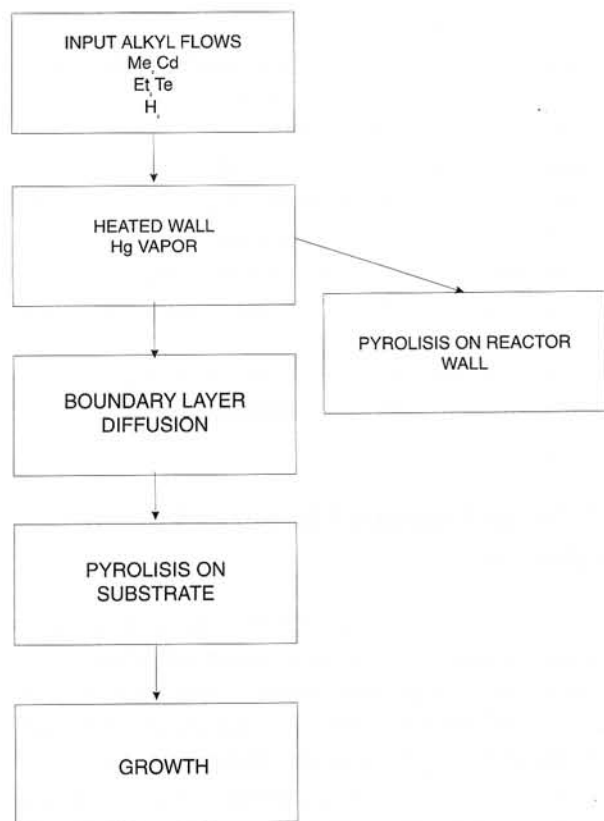


Fig. 4. Block diagram of transport processes which can affect layer composition (after Ref. 12).

transporting gaseous reactants to a reaction zones makes MOCVD a useful epitaxial technology. The formation of the desired compound occurs via pyrolysis of the organometallics, and subsequent recombination of the atomic or molecular species at or near the heated substrate. The process can be readily controlled by fixing the flow rates, and thereby the partial pressures of the various reactants, with electronic mass flow controllers. Similarly, complex multilayer epitaxial structures are readily formed by exchanging one gas composition or mixture for another by the use of automated gas-mixing systems. The pyrolytic nature of the reaction requires that only the substrate be heated to ensure efficient deposition. Fig. 4 shows the block diagram of transport processes, which can affect layer composition.

In summary, the growth of HgCdTe by MOCVD has been demonstrated at several laboratories, and the resulting structural and electrical properties have approached those found in LPE grown material. Recent progress in MOCVD growth of HgCdTe has been reviewed with emphasis on growth mechanisms and growth monitoring. A major advance in MOCVD has been the implementation of *in situ* optical diagnostics of the growing layer, giving information on growth

rate, composition and morphology [13]. This is providing new insights into the growth process and helping to identify causes of growth variance. Eventually this will form the basis of sophisticated *in situ* control of MOCVD reactors. Progress in doping HgCdTe layers has enabled the fabrication of p/n diodes which mirrors the success of the widely adopted p/n heterostructures grown by LPE over the vacancy doped n/p structure. MOCVD has the versatility to *in situ* passivate the epitaxial structure with CdTe. The MOCVD process also appears to be the easiest of the available epitaxial technologies to scale to production volume [14].

### 2.3. Molecular beam epitaxy

The vacuum deposition of HgCdTe by evaporation generally resulted in polycrystalline material because of the grossly incongruent vaporisation of HgCdTe. Recently, evolving technology has led to the growth of epitaxial layers of HgCdTe by MBE, laser evaporation and sputtering. Since its inception a two decades ago MBE has dominated the frontiers of material growth technology, has enabled the growth of a great variety of novel epitaxial layer structures, and allowed exact control over composition, doping, and thickness profiles. The use of MBE for HgCdTe, however, is complicated by the rapid and incongruent decomposition of HgCdTe, which occurs at elevated temperatures, and the high vapour pressure of Hg necessary to maintain stoichiometric integrity. These problems were successfully solved by Faurie et al, who reported the first epitaxial growth of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  on CdTe by MBE [15]. A schematic of the overall system is shown in Fig. 5. It consists of preparation and analysis chamber, a main MBE growth chamber, and a load lock for introducing and retrieving samples from either chamber. Because Hg has both a high vapour pressure and low sticking coefficient [16, 17], a special Hg MBE source is required. Ideally, the Hg source should be refillable without disturbing the UHV ambient of the main growth chamber and capable of generating vapour flux densities as large as  $10^{-3}$  Torr at the substrate during film growth. The Hg source designed and built at North Carolina State University is shown in Fig. 6. It consists of two Hg reservoirs and a heated tube separated by two UHV valves. Two fill (or refill) the Hg source, the internal Hg reservoir is first evacuated to UHV and then the valve between the reservoir and MBE chamber is closed. Next, Hg is introduced into larger external reservoir through the fill port. The valve between the two reservoirs is then momentarily opened so that Hg fills the internal reservoir. In this way, Hg is transferred to the



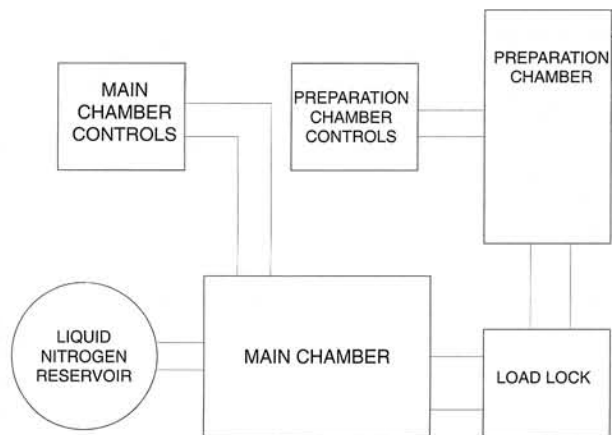


Fig. 5. Schematic of mercury compatible MBE system (after Ref. 21).

internal reservoir with minimum oxide contamination. The above source has been operational for more than 10 months. It has provided an extremely stable flux of Hg during film growth over long periods of use.

(111)GaAs, (111)Cd<sub>0.96</sub>Zn<sub>0.04</sub>Te, (100)CdTe and (111)Si wafers were used as substrates for MBE film growth. Immediately prior to the growth of a Hg-based film or multilayer, a CdTe buffer layer was deposited onto the substrate by MBE. Buffer layer thickness ranged from 2–10 μm.

Initially, MBE-grown layers were of poor structural and electrical quality, but with growth refinements epitaxial HgCdTe layers were obtained with significantly improved crystallinity and carrier mobility. Both n- and p-type layers were obtained by changing either the Hg flux or the growth temperature. For n-type layers with x = 0.20, the carrier concentration varied between 1.5 × 10<sup>15</sup> to 2 × 10<sup>16</sup> cm<sup>-3</sup>; for p-type samples the range was 2 × 10<sup>15</sup> to 2.5 × 10<sup>18</sup> cm<sup>-3</sup>. The highest carrier mobility obtained for n-type layer was 1.9 × 10<sup>5</sup> cm<sup>2</sup>/Vs, found in Hg<sub>0.80</sub>Cd<sub>0.20</sub>Te; for a p-type layer of the same composition it was 660 cm<sup>2</sup>/Vs. Low carrier concentration and high mobility were correlated

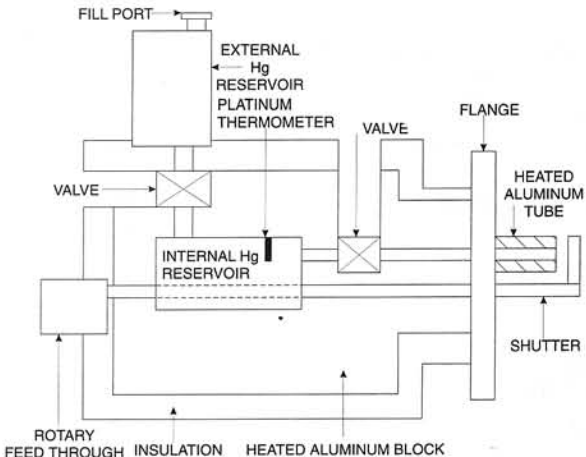


Fig. 6. Mercury MBE vapours source (after Ref. 22).

with high crystallinity. A photovoltaic device of medium performance was obtained in an as-grown Hg-CdTe using standard mesa and planar technology.

3. Summary

Table 1 illustrates some of the advantages and disadvantages of the three principal epitaxial growth techniques of HgCdTe.

Table 2 provides a comparison of state-of-the-art diodes reported elsewhere [18], and includes a comparison with InSb diodes [23].

LPE-grown HgCdTe was the first epitaxial material to equal and exceed the device performance of devices fabricated in bulk Hg<sub>1-x</sub>Cd<sub>x</sub>Te, and it also offered the additional benefits of large area, compositional uniformity, and reproducibility. While the device performance of MOCVD and MBE has not yet reached the LPE level, it is only a matter of time before parameters are established that will meet or exceed that goal, at least for some of those techniques.

Table 1. Comparison of HgCdTe epitaxial growth techniques

Growth technique	Advantages	Disadvantages
LPE	<ul style="list-style-type: none"><li>• High purity, ((2–20) × 10<sup>14</sup> cm<sup>-3</sup></li><li>• “Demonstrated” technology</li><li>• Production scale-up</li></ul>	<ul style="list-style-type: none"><li>◆ Melt retention problems (from Te-rich melts)</li><li>◆ Interface sharpness (2–3 μm)</li><li>◆ Multiple layers difficult</li></ul>
MOCVD	<ul style="list-style-type: none"><li>• Good surface morphology</li><li>• Sharp interfaces (&lt; 1 μm)</li><li>• Production scale-up</li></ul>	<ul style="list-style-type: none"><li>◆ Purity of starting materials</li><li>◆ Expensive equipment</li></ul>
MBE	<ul style="list-style-type: none"><li>• Composite structures, sharpest interfaces, superlattices</li><li>• Low growth temperature</li><li>• Good surface morphology</li><li>• In-situ analysis</li></ul>	<ul style="list-style-type: none"><li>◆ Expensive equipment</li><li>◆ Low growth rate</li><li>◆ Stringent substrate surface preparation required</li><li>◆ Marginal electrical properties</li></ul>

Table 2. Comparison of diode results at 77 K.

Material	Cut-off [ $\mu\text{m}$ ]	$R_{\text{OA}}$ [ $\Omega\text{cm}^2$ ]	Formation technique
LPE on CdTe (bulk THM)	4.6	$5 \times 10^6$ typical $2 \times 10^8$ best	Ion implantation
on CdTe/sapphire	4.6 5.1	$2 \times 10^6$ $2 \times 10^5$	
MOCVD on CdTe	5.3	$5 \times 10^4$ typical $8 \times 10^4$ best	
MBE on CdTe	5.1	$5 \times 10^4$ typical $7 \times 10^4$ best	Diffusion
InSb	5.5	$5 \times 10^6$	

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