

MOCVD growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ heterostructures for uncooled infrared photodetectors

A. PIOTROWSKI^{*1}, P. MADEJCZYK², W. GAWRON², K. KŁOS¹, M. ROMANIS¹, M. GRUDZIEN¹, J. PIOTROWSKI¹, and A. ROGALSKI²

¹VIGO System S.A., 3 Światlików Str., 01-389 Warsaw, Poland

²Institute of Applied Physics, Military University of Technology, 2 Kaliskiego Str., 00-908 Warsaw, Poland

We report here recent progress at VIGO/WAT MOCVD Laboratory in the growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ (HgCdTe) multilayer heterostructures on GaAs/CdTe and other composite substrates for uncooled infrared photodetectors. The optimum conditions for the growth of single layers and complex multilayer heterostructures have been established.

One of the crucial stages of the technology was CdTe nucleation on GaAs substrate. Successful composite substrates were obtained with suitable substrate preparation, liner and susceptor treatment, proper control of background fluxes and appropriate nucleation conditions.

The other critical stage is the interdiffused multilayer process (IMP). The growth of device-quality HgCdTe heterostructures requires complete homogenization of CdTe - HgTe pairs preserving at the same time suitable sharpness of composition and doping profiles. This requires for IMP pairs to be very thin and grown in a short time.

The practical implications for the IMP process are the CdTe/HgTe growth times that become comparable with transition times between the phases, characteristic for the MOCVD machine. The growth during transition stages is characterized by the non-optimum flow velocities and partial pressures that may induce poor morphology, reduce growth rate and cause other problems. This became especially acute for doped layers when large Cd/Te ratio is required for efficient incorporation and full activation of dopants. This has been solved by careful selection of hydrogen carrier gas and metalloorganics fluxes with suitable switching on and off times.

Arsenic and iodine has been used for acceptor and donor doping. Suitable growth conditions and post growth anneal is essential for stable and reproducible doping. In-situ anneal seems to be sufficient for iodine doping at any required level. In contrast, efficient As doping with near 100% activation requires ex situ anneal at near saturated mercury vapors.

As the result, we are able to grow multilayer fully doped (100) and (111) heterostructures for various infrared devices including photoconductors, photoelectromagnetic and photovoltaic detectors.

Keywords: MOCVD growth, $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ infrared photodetectors.

1. Introduction

The advanced photodetector architecture requires well establish epitaxial technology [1,2]. VIGO System S.A. has developed unique photodetectors for short, medium and long wavelength IR radiation operating without cryogenic cooling [2]. Development of this kind of devices led us to very fast devices optimized for one or more wavelengths with high responsivities.

Isothermal vapour phase epitaxy (ISOVPE) has been the base technology for $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ growth in VIGO System S.A for many years [3,4]. It is very mature and stable technique with a lot of limitations, however. Currently, ISOVPE is still used at Vigo System as a complementary technique to MOCVD. A combination of both techniques in many applications is also used.

Comparison of the epitaxial techniques used at VIGO System S.A. is shown in Table 1. One of the important advantages of metalorganic chemical vapour deposition (MOCVD) is the possibility to use the low cost composite substrates (GaAs , Si , sapphire) as the viable alternative to costly CdZnTe substrates. New generation high quality devices require $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ heterostructures with complex band gap and doping profiles. Those structures are difficult to grow with liquid phase epitaxy (LPE) or ISOVPE epitaxial techniques. Low temperature $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ growth with *in-situ* doping is possible for molecular beam epitaxy (MBE) and MOCVD techniques.

The main advantage of MBE is possibility to grow at the temperatures as low as 170°C . But post growth annealing at high temperatures is necessary for activation of an acceptor dopant.

MOCVD does not require high vacuum for growth, is easier serviceable technique with larger throughput. Last,

* e-mail: apiotrow@vigo.com.pl

Table 1. ISOVPE vs. MOCVD.

Parameter	ISOVPE	MOCVD
Growth temperature	500°C	320–370°C
Substrates:	CdZnTe	GaAs, sapphire, silicon
cost	< \$100/cm ²	< \$20/cm ²
availability	limited, small wafers	large area available
mechanically	soft	hard
thermal conductivity	low	high
Uncontrolled doping	$\approx 1 \times 10^{15}$ cm ⁻³	< 1×10^{15} cm ⁻³
Composition profiles	Graded profiles only	With soft and sharp interfaces
Doping during growth	Difficult	Easy
Doping profile	Difficult	Easy
Throughput	≈ 100 cm ² /month	> 1000 cm ² /month
Equipment cost	\approx \$0.1 M	\approx \$1 M

but not least, donor and acceptor doping at medium and high level, essential for near room temperature devices, is simpler with MOCVD. That is why for our purposes we choose the Aixtron Aix-200 II–VI MOCVD system. Fast switching valves, high quality materials and proper reactor design allow us to run fully computer controlled processes. Low to atmospheric pressure growth is possible. Drawback of this technique is high cost of equipment and high toxicity of precursors which is prevented by an advanced safety system.

The MOCVD system was installed in March 2003. The laboratory infrastructure was constructed from the ground in cooperation of VIGO System S.A. and the Military University of Technology. It took half a year to develop CdTe buffer layer technology. In November 2003, fully doped heterostructures for devices became available. Since then we have developed optimum growth parameters for the devices covering the whole 2–16 μ m range. Until August 2004, we grew over 380 heterostructures. Most of them were experiments on fundamental growth parameters, only small percent of all runs was useful for production purposes.

2. MOCVD system

Aixtron Aix-200 II–VI MOCVD system is a horizontal reactor customized for $Hg_{1-x}Cd_xTe$ growth on 2" wafers (Fig. 1). Inlet is on the left side. Pd-cell purified hydrogen is used as carrier gas. Between the processes system is filled with nitrogen fined by getter purifier. Liquid nitrogen is used as the nitrogen source.

Dimethylcadmium (DMCd), diisopropyltelluride (DIPTe) and diethylzinc (DEZn) used as precursors are held at the temperature stabilized baths. Elementary mercury is held in quartz container in the lower input channel of the container.

AsH₃ has been used for arsenic precursor. The drawback of arsine is its toxicity. Special safety preventive measures must have been applied to the laboratory.

Ethyl iodide (EI) is used for donor doping. Because of its high vapour pressures [5], the metalorganic source for iodine must be held at low temperatures (< 5°C).

DMCd/EI and DIPTe/AsH₃ input channels are separated by partition to prevent premature gas mixing and dust formation. In lower channel a mercury container is placed. Evaporating mercury is carried out by hydrogen to the growth zone. Drawback of this solution is dissolution of Te and As sources in the elementary mercury container. This may result in As memory effects. The surface of the mercury is covered with black skin, probably HgTe after deposition causing growth instabilities.

Hydrogen from the upper channel dilutes mercury saturated hydrogen from the lower channel. Therefore, decreas-



Fig. 1. Aix-200 II–VI system installed at VIGO/WAT MOCVD Laboratory.

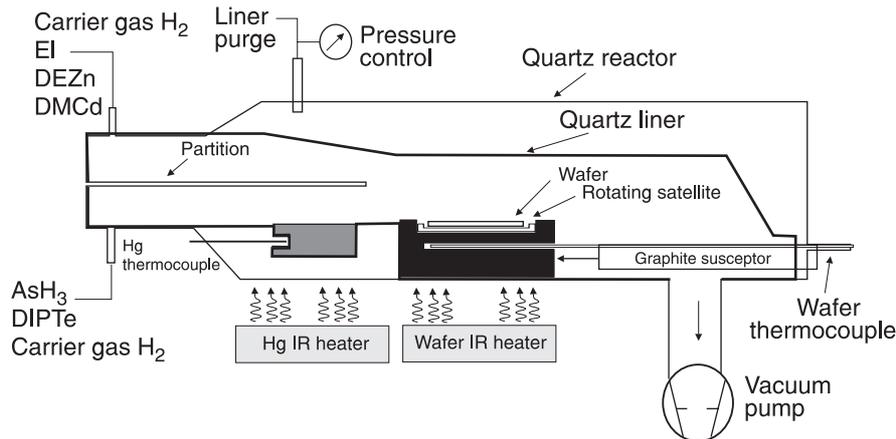


Fig. 2. Schematic drawing of Aix-200 II-VI reactor.

ing of the mercury partial pressure over the wafer must be taken into account and it can be altered by changing the lower to upper channel flow ratio. In practice flow is selected separately for each phase; for example 100/500 sccm or 1200/1200 sccm flow ratios have been used. In this notation first number is mass flow in the upper channel and the former is mass flow in the lower channel.

In a reactor there are two temperature zones: the mercury source zone (up to 300°C) and the growth zone with a graphite susceptor (up to 900°C). Reactor temperatures of 360–410°C have been used and mercury have been held at 200–220°C. Higher temperatures are used for reactor cleaning.

A substrate is laying on a rotating disk using Aixtron's gas foil rotation technique. A vacuum system provides the possibility to keep reactor in the pressures from 50 mbar to atmospheric pressure. The reactor pressure of 500 mbar was used for all successful growth runs.

MOCVD system contains explosive materials such as hydrogen and toxic materials as AsH_3 , mercury and metalorganics precursors. Therefore, laboratory is equipped in advanced safety features such as hydrogen, arsine and mercury detectors, very effective ventilation system and different safety interlocks embedded in the Aixtron's system (see Fig. 2). Large quantities of mercury are being transported during growth. They are condensed at low temperature Hg trap. Glovebox nitrogen atmosphere contains a lot of mercury and all its gas outlets are equipped in activated coal filters. All toxic gases are neutralized in the wet scrubber system.

3. CdTe buffer growth

CdTe buffer growth on GaAs is probably the most critical stage in HgCdTe growth due to lattice mismatch. For GaAs and CdTe, the mismatch is approximately 14.3%. So, huge mismatch is neutralized by 2–10- μm thick CdTe buffer. The buffer plays also role of Ga diffusion barrier [6].

Careful chemical and thermal treatment of the reactor must be carry out after each grow run to prevent residual

deposits of HgCdTe on substrate that adversely affect nucleation stage of growth. Different phases on the edges and in the middle of the wafer were frequently observed for poorly cleaned reactor.

Epiready (100) GaAs wafers with 2–4° disorientation towards nearest $\langle 100 \rangle$ and $\langle 110 \rangle$ have been used. Due to the large mismatch between GaAs and CdTe, both (100) and (111) growth may occur. It mostly depends on substrate disorientation and preparation, nucleation conditions and growth temperature. Cd or Te substrate treatment just before growth results in (100) and (111) orientation, respectively.

Generally, the layers with orientation (100) shows superior morphology compared to (111) (Figs. 3 and 4) but

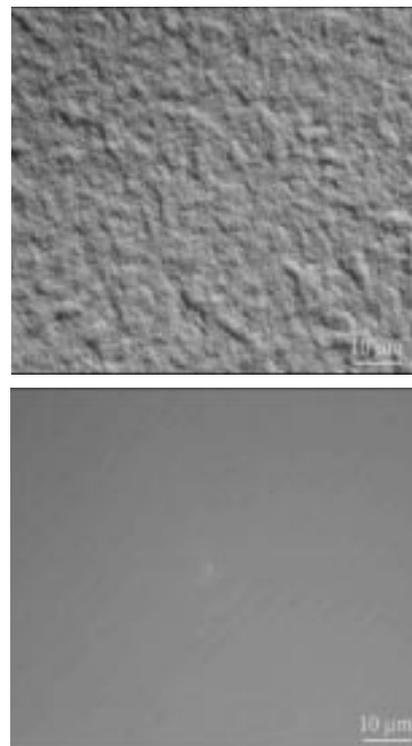


Fig. 3. Surface morphology of (111) and (100) layers.

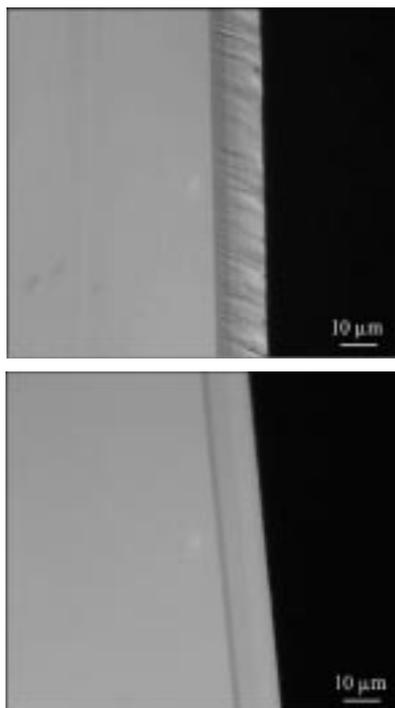


Fig. 4. Cleavages of (111) and (100) layers.

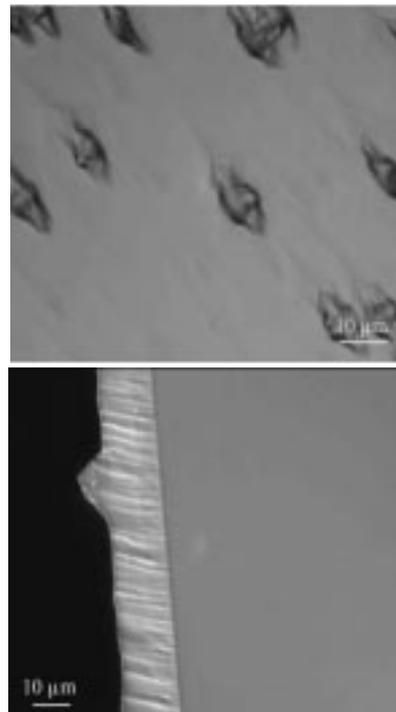


Fig. 5. Hillocks on (100) layers: top view and cleavage.

they are also characterized by hillocks (Fig. 5). Height of hillocks is typically twice higher compared to the layer thickness.

Origin of hillocks is not fully understood at present. Hillocks are created during CdTe buffer growth and HgCdTe growth only enlarging them. Epilayers with hillocks are practically useless for device fabrication. Various ways to prevent hillocks formation have been tried: Zinc nucleation layer, different Cd/Te ratios, different substrates orientations have been used, but we were able to grow hillocks-free layers only on some substrates from one supplier. Therefore, most of the devices were based on (111) layers.

4. $Hg_{1-x}Cd_xTe$ growth

Direct $Hg_{1-x}Cd_xTe$ growth is difficult due to different thermodynamic properties of HgTe and CdTe [5,7]. We applied interdiffused multilayer process (IMP) for $Hg_{1-x}Cd_xTe$ growth to avoid this problem. IMP gives possibility for controllable growth of heterostructures with complex composition and doping profiles. HgTe and CdTe layers are deposited one after another with period 100–200 nm and homogenized by interdiffusion during growth. Any composition can be achieved in this way by proper selection of HgTe and CdTe layer growth times.

Significant delays in delivery of precursors to the growth zone and mixing effects result in adverse transient states between CdTe and HgTe phases. This may be prevented by introduction of flush stages between the CdTe and HgTe phases to separate completely both growth phases and let all precursors from the former stage to leave the growth zone. Flush length is selected intentionally after

series of calculations and experiments to assure that all precursors are delivered before the end of each flush. Because of different precursor's flow moment of opening, each precursor must be shifted compared to each other.

Figure 6 shows the changes of Hg, Te and Cd partial pressures in the growth zone during four phase IMP growth. Sources are opened at the beginning and locked at the end of the CdTe or HgTe phases. Plug flow model is used to calculate the delays. This model does not take into account mixing effects.

Optimum parameters for the four stages IMP growth have been found. To optimize distribution of precursors's pyrolysis, linear velocity of carrier gas and partial pressures must be selected separately for each phase.

Decomposition of DIPTe, tellurium precursor without DMCD is much less efficient than with Cd precursor at

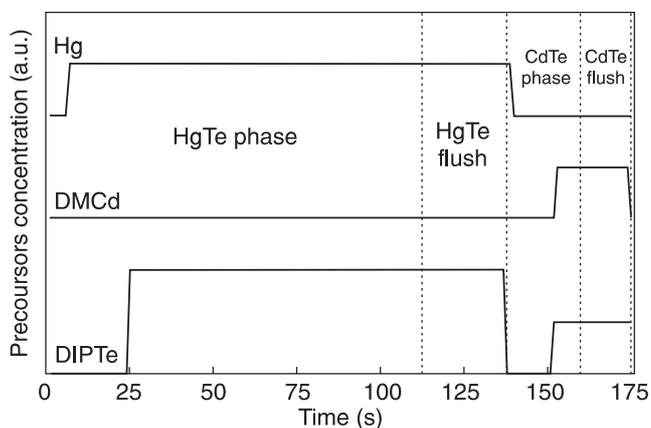


Fig. 6. Kinetics of the precursor delivery to the growth zone.

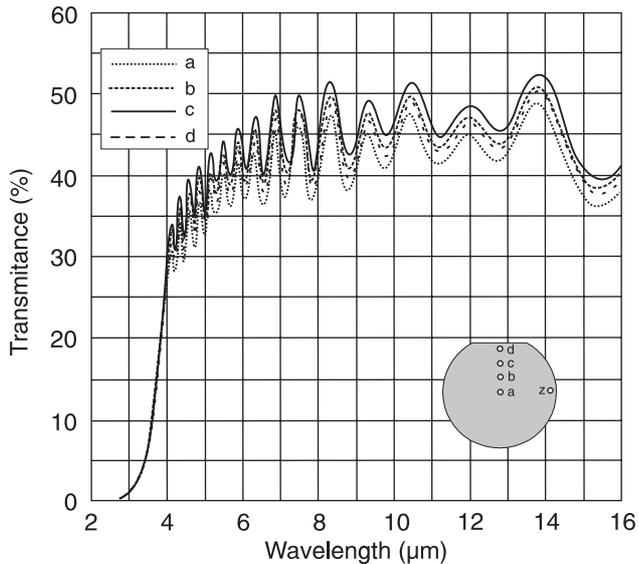


Fig. 7. Infrared transmission spectra of the multilayer heterostructure.

growth temperatures. To increase decomposition rate, low velocity of carrier gas is used (approx. 2 cm/s). To assure high mercury concentration lower flow in upper channel then in lower channel has been used (200/600 sccm or 100/500 sccm). Low flow and high Hg and DIPTe concentration gives HgTe growth rate approx. 5 $\mu\text{m}/\text{h}$.

Decomposition of DIPTe in presence of DMCD is more efficient and higher carrier gas flow (approx. 8 cm/s) is used for CdTe and CdTe flush stages. This stage is very important because it is when dopants incorporate. Growth rate for this stage depends on dopants partial pressures over the wafer and varies from 5–8 $\mu\text{m}/\text{h}$. Equal flows (1200/1200 sccm) in each channel have been applied to assure laminar flow, better gas mixing and on-wafer uniformity.

Figure 7 shows transmission of HgCdTe epilayers. The absorption edge is mostly determined by the layer with the lowest x -value and can be used to determine a composition. We can evaluate composition uniformity across the wafer by mapping. The compositional uniformity over the wafer as low as $\pm 0.1\%$ is achieved.

The infrared transmittance spectra of high quality layers are close to the theoretical ones. This is an evidence of good in-depth homogeneity. Complex interferences patterns are observed for long wavelength.

Compositional profiles were evaluated for some samples by differential reflection spectra or with SIMS method.

5. Hg_{1-x}Cd_xTe doping

5.1. Undoped layers

Electrical properties of nominally undoped Hg_{1-x}Cd_xTe layer are determined by native acceptors (metal vacancies) and uncontrolled background doping. Vacancy concentration strongly depends on reactor temperature, vapour pres-

sure and material composition. The native doping level after growth at 360°C with mercury temperature 200°C is approximately $5 \times 10^{16} \text{ cm}^{-3}$. This is much below the expected level of $> 1 \times 10^{17} \text{ cm}^{-3}$ for these temperature conditions [7]. We suspect that it is due to partial annihilation of vacancies during cool down. It could be influenced by hydrogen presence in the layer.

The vacancy concentration can be changed by post-growth annealing in mercury vapours. Vacancies may be practically eliminated by a prolonged, low temperature ($\approx 200^\circ\text{C}$) annealing at near saturated mercury pressures. Such annealing reveals the background doping level. We have observed that the uncontrolled background for our MOCVD system was about $N_d - N_a = (1-3) \times 10^{15} \text{ cm}^{-3}$.

Ex-situ anneal in sealed quartz ampoules in mercury vapours is typically used to maintain isothermal conditions. This technique is not practical for production purposes. Instead, we developed more convenient *ex-situ* anneal technique in which a wafer after growth was transported into reusable quartz container. The temperatures up to 400°C and Hg pressures up to 2 bars could be used.

High and low temperature annealing was used. Typically, a short (approx. 20min–3h) high temperature (360°C) anneal was used for doping homogenization followed by long (> 2 h) low temperature (250°C) anneal for vacancy annihilation. Mercury pressure has been changed during both stage of this annealing to maintain conditions close to isothermal.

In-situ annealing is very practical for production purposes. This eliminates need for any “hot” processes after removal of wafers from the MOCVD reactor, and possibilities to introduce additional impurities.

We have developed *in-situ* annealing technique which can be applied for many practical purposes. The annealing is carried out in the reactor immediately after the growth.

When the growth is finished, the temperature of the wafer is gradually lowered to 210°C in 1–6 hours keeping the mercury source temperature at the 200–220°C. After that both reactor and mercury are cooled down. It must be avoided to cool down the reactor below the mercury level to prevent Hg droplet formation. During annealing it is not possible to close the reactor and stop a hydrogen flow. This result in significant mercury losses. In practice, this means that we cannot obtain near saturated mercury pressures at the temperatures $> 220^\circ\text{C}$. This effect can be limited by selecting optimal upper to lower channel flow ratio.

Vacancy and background doping is not sufficient for advanced infrared devices that require donor and acceptor doping at medium and high doping levels.

5.2. Doping with foreign impurities

Iodine and arsenic have been used as foreign dopants. Both are well-behaved, stable and slowly diffusing dopants. To be active dopant they must occupy Te sites. Therefore, metal-rich conditions are favourable for iodine incorporation and required for arsine. Therefore, they are introduced

during CdTe phase with Cd/Te ratio >1 . Most of doping experiments have been carried out for (111) $Hg_{1-x}Cd_xTe$ layers.

5.2.1. Iodine doping

Iodine is well behaved dopant and is typically used to obtain heavily doped n^+ -layers. Therefore, it is important to establish the conditions for iodine doping at $>10^{17} \text{ cm}^{-3}$ level. Cd/Te ratio of 1.1–1.3 has been used during CdTe phase to improve efficiency of I incorporation and activation. It allows doping concentration between 1×10^{17} and $1 \times 10^{18} \text{ cm}^{-3}$ for compositions about 0.3.

The concentrations exceeding 10^{17} cm^{-3} has been obtain with EI fraction of 10 ppm and our standard *in-situ* anneal. Improved efficiency of doping has been observed with *ex-situ* annealing at 360°C at near saturated mercury pressures. This effect may be related to incomplete iodine homogenization during growth and *in-situ* annealing, since iodine diffusion is very slow (noticeably slower than Cd diffusion into HgTe).

No or insignificant I doping memory effects has been observed. Good reproducibility of I doping has been observed.

5.2.2. Arsenic doping

Arsine incorporation into Te sites is very sensitive for metallic rich conditions. This assures conditions for arsenic to enter Te sites where it acts like acceptor. Otherwise arsenic can show amphoteric behaviour.

High doping concentrations ($>5 \times 10^{17} \text{ cm}^{-3}$) have been achieved in higher x materials ($x > 0.25$) with Hg temperature 220°C and arsine fraction of 10 ppm. It is much more difficult to achieve heavily doped low x materials. The concentrations up to $2 \times 10^{17} \text{ cm}^{-3}$ have been achieved for mercury temperature of 220°C , Cd/Te ratio equal to 3 and arsine fraction of 10 ppm in the growth zone.

Ex-situ isothermal annealing in high mercury vapours ($360/350^\circ\text{C}$) shows significant effects on acceptor doping. It is probably related to arsenic activation in the material.

Strong dependence of CdTe growth rate was visible for different arsine concentrations. It is between 4 and 8 $\mu\text{m/h}$ and it strongly depends on dopants partial pressures.

6. Conclusions

Practical implementation of the advanced photodetector architecture requires well established epitaxial technology. In

Poland, for a long time, the isothermal vapour phase epitaxy (ISOVPE) in reusable growth system was used in VIGO System S.A. to grow HgCdTe heterostructure devices. Now, the ISOVPE has been replaced with MOCVD (a common investment of VIGO System and Military University of Technology, Warsaw). This technique has been selected for its inherent versatility (low growth temperature, ability to grow layered structures with complex composition and doping profiles while maintaining sharp interfaces). MOCVD makes possible to use low-cost and high quality substrates (GaAs, sapphire and silicon), has the potential for a large-scale production and is cost-effective. Physical properties of MOCVD HgCdTe heterostructures on GaAs substrates exceed those on costly CdTe substrates.

HgCdTe heterostructures have been grown on $2''$ (100)GaAs. Reproducible n- and p-type doping at the low, intermediate and high level (10^{15} – 10^{18} cm^{-3}) has been achieved with stable iodine and arsenic dopants. The dopants are easily activated during growth in contrast to MBE. This technology is used for photoconductive, photoelectromagnetic, and photovoltaic HgCdTe devices.

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