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Uncooled infrared photodetectors in Poland

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The history and present status of the middle and long wavelength $Hg_{1-x}Cd_xTe$ infrared detectors in Poland are reviewed. Research and development efforts in Poland were concentrated mostly on uncooled market niche.

Technology of the infrared photodetectors has been developed by several research groups. The devices are based on mercury-based variable band gap semiconductor alloys. Modified isothermal vapour phase epitaxy (ISOVPE) has been used for many years for research and commercial fabrication of photoconductive, photoelectromagnetic and other devices. Bulk growth and liquid phase epitaxy was also used. At present, the fabrication of IR devices relies on low temperature epitaxial technique, namely metalorganic vapour phase deposition (MOCVD), frequently in combination with the ISOVPE.

Photoconductive and photoelectromagnetic detectors are still in production. The devices are gradually replaced with photovoltaic devices which offer inherent advantages of no electric or magnetic bias, no heat load and no flicker noise. Potentially, the PV devices could offer high performance and very fast response. At present, the uncooled long wavelength devices of conventional design suffer from two issues; namely low quantum efficiency and very low junction resistance. It makes them useless for practical applications. The problems have been solved with advanced 3D band gap engineered architecture, multiple cell heterojunction devices connected in series, monolithic integration of the detectors with microoptics and other improvements. Present fabrication program includes devices which are optimized for operation at any wavelength within a wide spectral range 1-15 μm and 200–300 K temperature range. Special solutions have been applied to improve speed of response. Some devices show picoseconds range response time. The devices have found numerous civilian and military applications.

Keywords: infrared photodetectors, uncooled detectors, photovoltaic detectors, heterostructures.

1. Research on $Hg_{1-x}Cd_xTe$ and related IR devices

The discovery of photoelectrical properties of $Hg_{1-x}Cd_xTe$ (MCT) by British scientists [1] triggered immediate start of Polish efforts in the field. Numerous institutions have been involved in the basic research and development of $Hg_{1-x}Cd_xTe$ infrared devices for the last four decades.

The $Hg_{1-x}Cd_xTe$ studies began in 1960 at the Institute of Physics of the Polish Academy of Science (IFPAN), Warsaw [2–5]. Bridgman technique with sealed thick wall quartz ampoules was used to grow material suitable for research and experimental devices. The explosions caused by the high mercury pressure were quite frequent that time, resulting in a few series accidents. The grown material was used for optical and galvanomagnetic studies. The studies were aimed at determination of energy band structure of the material. The $Hg_{1-x}Cd_xTe$ studies were for a long time the main topics of numerous meetings on solid state physics and electronics in Poland. The studies were important contribution to the understanding of fundamental properties of the material.

Simple photoconductive, photoelectromagnetic and photovoltaic devices based on the bulk MCT crystals were demonstrated already in 1963 [6]. Interesting, the first photovoltaic devices were based on n-on-p junctions that were formed at perimeter of MCT ingots during cool down period. Later, IF PAN scientists concentrated their efforts on diluted magnetic semiconductors such as $Hg_{1-x}Mn_xTe$, less useful for infrared photodetectors.

In 1968, device-oriented research started at the Military University of Technology (MUT), Warsaw. The development until 1985 was reviewed in the book [6], we will remind here the main results. From the very beginning the research was concentrated on epitaxial growth. Initially, a modification of the Isothermal Vapour Phase Epitaxy (ISOVPE), discovered by Cohen-Solal *et al*. [7] in France, was applied. The original process relies on near-equilibrium isothermal evaporation of HgTe upon a thick CdTe substrate [Fig. 1(a)]. Interdiffusion of the grown layer with the substrate yields variable gap structures.

In the Polish modification [8] (Fig. 1b), the composite thin CdTe layers were used rather than the bulk CdTe. The layers had been deposited by vacuum evaporation on low-cost and readily available substrates such as mica, silicon, sapphire and other. Limited amount of HgTe was then deposited by ISOVPE and the process was carried out up to

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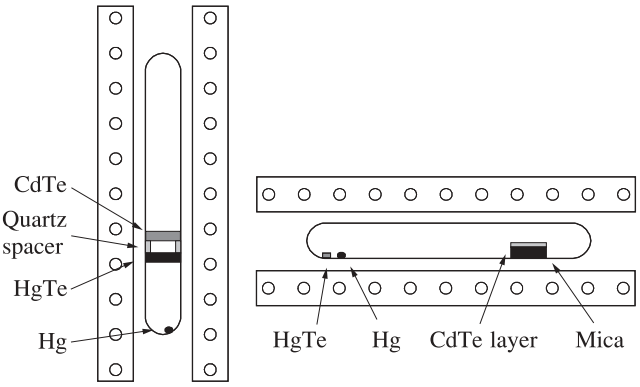

Fig. 1. ISOVPE growth in sealed ampoules: (a) original ISOVPE technique and (b) Polish modification.

complete homogenization. As the result, extremely uniform epitaxial layers were grown.

The layers were used as the basis for fabrication of photoconductive, photoelectromagnetic and photovoltaic detectors operating in the MWIR and LWIR range at near room temperature [6,8–11]. The first long wavelength (≈10.6 μm) detectors operating at high temperatures ("HOT" detectors) were demonstrated already in 1972 [6,9]. They were probably the first commercially available, epitaxial $Hg_{1-x}Cd_xTe$ detectors grown on hybrid substrates. Interesting, the first user of the devices was the Los Alamos Lab., USA where the devices were applied for laser fusion experiments.

Bulk growth had also been tried. For this purpose, a modification of the quench-anneal technique was developed in which the quenched ingot was annealed in temperature gradient perpendicular to the axis of the ingot [12–14]. Uniform and high quality $Hg_{1-x}Cd_xTe$ and $Hg_{1-x}Zn_xTe$ crystals have been grown. They were used both for studies of the material properties and for practical IR devices. The other subjects of the research were p-to-n conversion with ion implantation, ion milling and anodic oxidation of $Hg_{1-x}Cd_xTe$ and other Hg-based materials [15,16].

The need for complex multilayer heterostructures for high quality infrared devices, especially those operating at near room temperature devices, has been recognized. Initially, buried N-p junction photodiodes grown by ISOVPE were used to reduce dark current in photodiodes [17]. Later, hot wall epitaxy [18] and the LPE [19] growth from Te-rich solution has been also tried.

The MUT's group is also known for detector modelling [20], studies of fundamental problems of the infrared detection [21] and, especially, for numerous Rogalski books and excellent review papers on infrared detectors [22–29].

Significant efforts on $Hg_{1-x}Cd_xTe$ detectors were at Wrocław Technical University. The sealed ampoule ISOVPE technique had been used for a long time. Graded gap layers growth by this technique was extensively studied [30–35]. High quality photovoltaic devices with n-on-p junction formed by Hg in-diffusion had been demonstrated. This group was near to commercialization of the liquid nitrogen cooled photovoltaic devices, but eventually failed to achieve the goal. The main problem was limitation of the conventional sealed ampoule technique- low productibility, lack of extrinsic doping and passivation techniques.

The $Hg_{1-x}Cd_xTe$ related research has been carried out also at the Institute of Electron Technology, the Institute of Vacuum Technology, Rzeszów University of Technology, the Military Institute of Armament Technology and many other institutions. Extensive studies of photoelectromagnetic effect in $Hg_{1-x}Cd_xTe$ have been carried out at Silesian Technical University [36].

2. Commercialization of the infrared detectors at VIGO System

The commercialization of the infrared detectors in Poland started in the early 1980's, initially at the Institute of Plasma Physics and Laser Microfusion and then at the medium size company VIGO System S.A., Warsaw. The niche market strategy has been pursued with main goal of the versatile production of the uncooled infrared photodetectors optimized for operation at any wavelength within the short, middle, and long wavelength range of infrared spectrum.

Significant development efforts were necessary. Despite many years of R&D, no economically efficient technology suitable for the growth of the base material was available that time. Initially, the existing bulk growth and ISOVPE epitaxy in sealed ampoules was used. The techniques were inconvenient and costly, however.

2.1. Open tube ISOVPE growth

The solution was the open tube growth. A unique production-type atmospheric pressure system was developed in cooperation with Djuric's group from Belgrade University [37,38]. The epitaxial system (Fig. 2) allows several large area layers to be grown in one growth run. Mercury loss was reduced to a few milligrams for one growth run by the use of quartz container with a conical quartz plug. The sys-

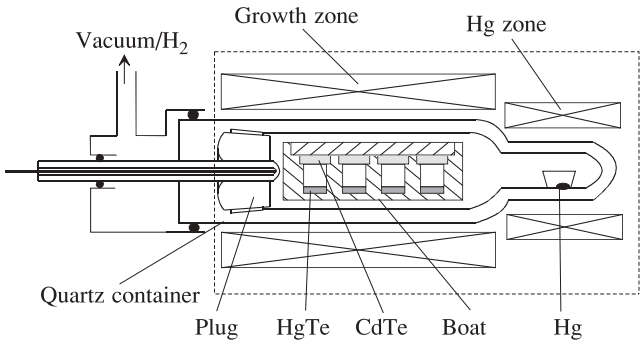

Fig. 2. Isothermal vapour phase growth reactor. Low cost polycrystalline HgTe sources and large grain CdTe (or CdZnTe) substrates are used.

tem had two independently controlled temperature zones: the mercury zone (20–400°C) and the growth zone (20–580°C). Typically, it took less than two hours to grow a complete device heterostructure. For a good lateral uniformity ($\Delta x < 0.005$), variation of the temperature in the growth zone should be less than 0.3 K. In-depth band gap profiles have been shaped in controlled way by variations of growth conditions and subsequent post-growth annealing. The necessary growth conditions can be theoretically predicted using computer simulation of ISOVPE based on generalized model of the process [39].

Layers with the thicknesses from < 1 μm to > 1 mm and the surface compositions $0 < x < 1$ could be obtained, in dependence on growth conditions. Typical in-depth compositional profiles are shown in Fig. 3. As-grown epilayers exhibit a significant grading. If the growth stage is followed by the heat treatment at temperatures lower than the deposition temperatures (300–400°C) with deposition suppressed by increased mercury vapour pressure, nearly uniform composition in the most part of the layer (≈2/3 of total thickness) could be obtained. A significant grading in the bottom portion of the layer occurs, however. In addition, post-growth thermal processing (e.g. "negative epitaxy") could be used to widen the band gap of the near surface region.

To reduce concentration of vacancies the process is completed with programmed cooling down the growth and mercury zones to room temperature. Low 10^{15} cm^{-3} electron concentration has been typically obtained. The relatively high carrier concentrations probably results from impurities either in the substrates, source materials, gases, or contaminants on the substrate surface.

Initially, the doping level was controlled by heat treatment in mercury vapour to establish the resulting concentration determined by the difference between concentration of native acceptors and residual donor impurities. Later, the required doping was achieved by extrinsic doping (In, Au and As). Basic material for the near room temperature devices is lightly doped p-type layers. As and Au dopants are introduced into epilayers *in-situ* during growth. This approach integrates growth and device fabrication. Some devices were *ex-situ* processed, doped by diffusion or/and ion milling.

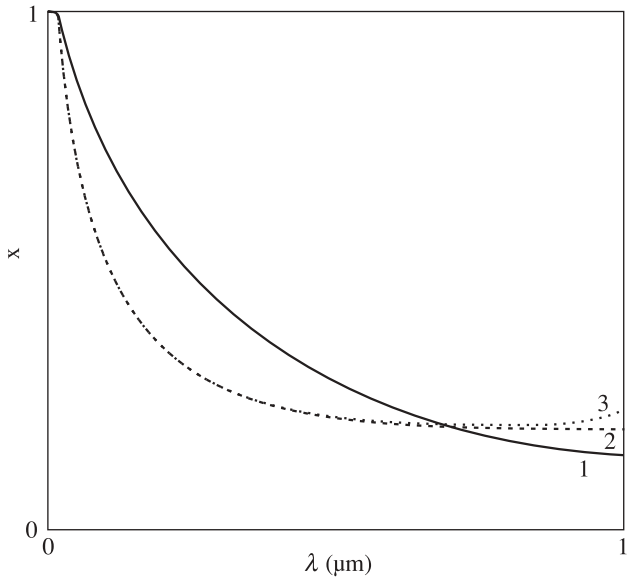

Fig. 3. Compositional profiles of epilayers obtained by ISOVPE: 1 – as grown, 2 – after heat treatment, and 3 – after post growth processing.

In contrast to the low temperature epitaxial techniques (LPE, MOCVD and MBE), ISOVPE yields smooth surface morphology, independently on substrate orientations (for growth temperatures T > 500°C). Therefore, non-oriented or large grain polycrystalline CdTe (or CdZnTe) substrates are typically used. The other choice is composite substrates–mica, GaAs, sapphire, silicon and other.

The HgTe source are polycrystalline wafers used for many growth runs (> 15). In general, the technique is characterized by a very low consumption of starting materials – mercury, tellurium and cadmium, probably less than for any other $Hg_{1-x}Cd_xTe$ growth technique.

Three-dimensional band gap profiling is necessary to optimize near room temperature photodetectors [40,41]. Several methods have been used to modify in depth and lateral band gap profiles.

Selective epitaxy

Selective epitaxy can be achieved by ISOVPE onto substrates partially masked with SiO_x layers (Fig. 4). SiO_x layer prevents epitaxy on covered substrate since interdiffusion between substrate and growing layer is blocked. Residual deposition at borders of exposed regions is due to lateral interdiffusion. A characteristic feature of the selective ISOVPE is a decreased fraction of CdTe in the border regions.

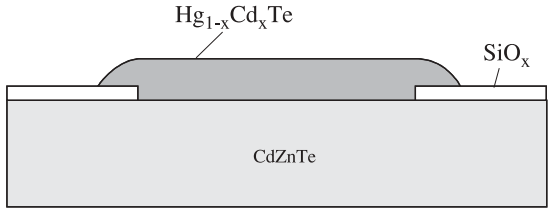

Fig. 4. Schematic cross-section of epilayer obtained by selective ISOVPE.

Epitaxy on profiled CdTe substrates

In this method, the ISOVPE growth is carried out onto CdTe substrate with etched off some regions (Fig. 5). Next, the substrate is mechanochemically polished to obtain flat surface with immersed $Hg_{1-x}Cd_xTe$ pockets. This technique produces epilayers with increased fraction of CdTe in border region which is important for some devices.

Negative epitaxy

This is reversed ISOVPE process based on quasi-equilibrium isothermal evaporation of HgTe from previously deposited $Hg_{1-x}Cd_xTe$ epilayer. The process is performed in hydrogen atmosphere at relatively low temperatures (300–

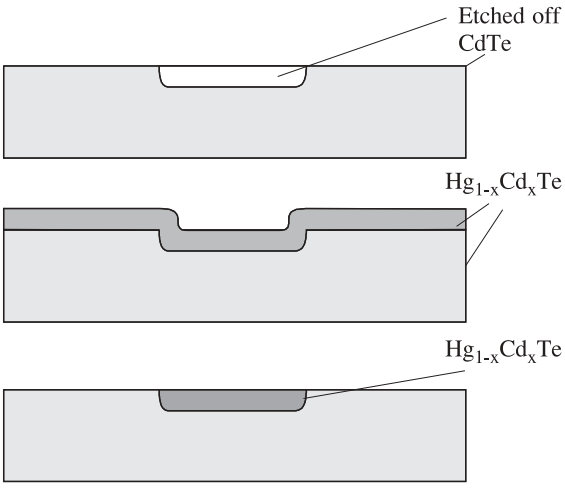

Fig. 5. Epitaxy on profiled CdTe substrates.

400°C) which results in increased fraction of CdTe (Δx = 0.01–0.10) in the surface region of epilayer. We use extensively this technique to widen band gap of surface region of mesa $Hg_{1-x}Cd_xTe$ structures. Resulting, relatively sharp, compositional profiles have been measured. Good overall agreement has been found with theoretical prediction based on the computer simulations of ISOVPE. To obtain a wide gap and heavily doped surface region, the negative epitaxy has been often combined with As doping from gas phase.

Post growth deposition of CdTe or CdTe/ZnS

Deposition of CdTe is a very efficient method of passivation of $Hg_{1-x}Cd_xTe$ devices. Unfortunately, CdTe cannot be deposited *in situ* by ISOVPE. CdTe layers can be deposited by thermal evaporation or sputtering. The main problem is formation of unstable oxides layer on $Hg_{1-x}Cd_xTe$ which may adversely affect surface properties. Chemical surface treatment immediately before deposition has been used. In practice, CdTe/ZnS layers were used mostly for final passivation of the devices while the passivation of absorber regions was typically achieved by widening of band gap of near surface region with negative epitaxy.

2.2. MOCVD growth

The M-ISOVPE technique was not very useful for growth of multiple layer heterostructures with complex composition and doping profiles that are required for the most advanced IR photodetectors. In 2003, VIGO System and MUT established common MOCVD laboratory with AXT 200 II-VI dedicated system. Since then MOCVD technology and related devices have been developed. The present status is described in Refs. 42 and 43. Successful growth of multilayer heterostructures has been demonstrated on CdTe, GaAs and other substrates. Numerous improvements have been introduced such as online control of precursor delivery, stoichiometry adjustment during growth and final growth stage procedures to obtain low vacancy material with required n- or p-type doping without and post-growth thermal processing.

2.3. 3D Heterostructure photodetector concept

In the early 1900's, VIGO System recognized fundamental limitations to performance of the infrared detectors imposed by unavoidable physic of the thermal generation and the ways to perfect detection with HOT detectors [11, 44–47].

The general expression for maximum detectivity of the optimized detector of any type was derived [48]:

$$D^* = 0.64k\left(\frac{A_o}{A_e}\right)^{1/2}\left(\frac{\alpha}{G}\right)^{1/2}$$

The ratio of absorption coefficient to the bulk thermal generation rate, α/G, is the basic figure of merit of any semiconductor material for infrared photodetector. A_o/A_e is the ratio of the optical to physical area of the detector. The coefficient k reflects the influence of reflectance at the front and back surface of the detector. The maximum value of k is achieved for 0 and 1 reflectance at the two surfaces (no interference). Further gain in k can be obtained with enhanced absorption in thin absorbent by the use of optical resonant cavity.

According to these considerations, 3D heterostructure concept of a photodetector (3DHC) was developed to maximize the basic k, A_o/A_e, and α/G terms and minimize non-fundamental parasitic effects. Integration of optical, detection, and electronic functions in one heterostructure chip (Fig. 6), such as concentration of optical radiation to increase A_o/A_e, enhanced optical absorption and effective collection of photogenerated charge carriers was assumed.

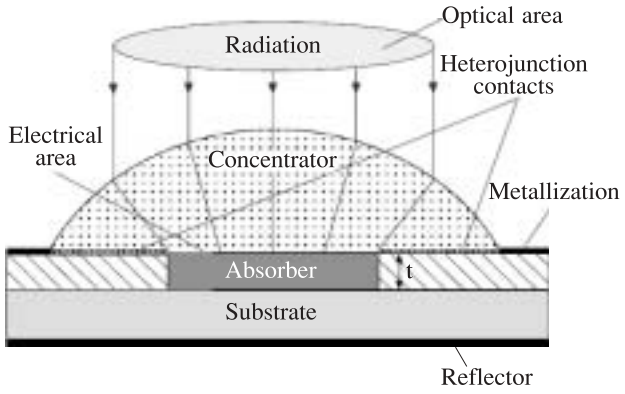

Fig. 6. Schematic illustration of the 3D heterostructure photodetector.

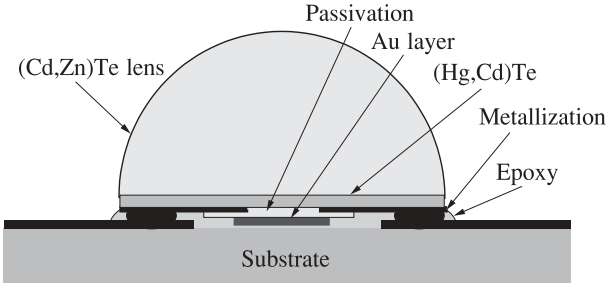

Fig. 7. Structure of advanced monolithic optically immersed photoconductor. The active element is supplied with a gold back reflector.

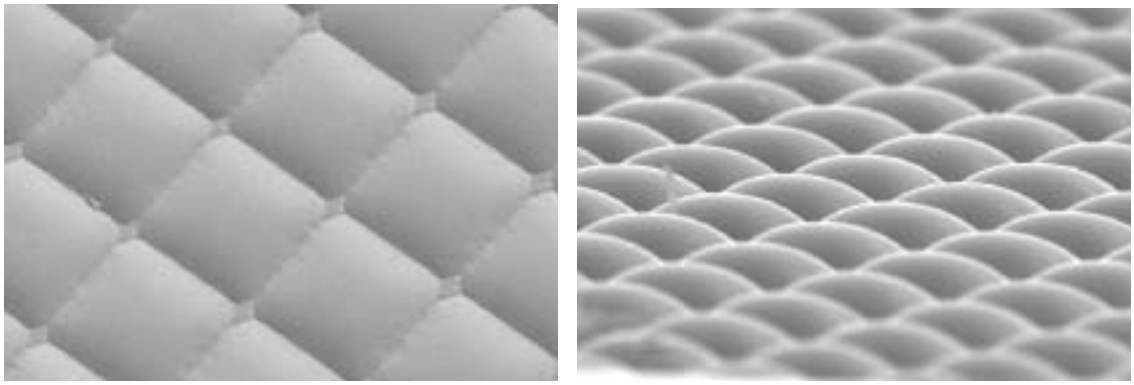

Fig. 8. Arrays of 50-μm pitch microlenses, the top and tilted side view.

The 3DHC concept has been gradually developed and implemented [48,49]:

- the absorber band gap, composition and thickness have been optimized for the best compromise between requirements of efficient use of IR radiation low thermal generation,
- heavily n and p-type doped $Hg_{1-x}Cd_xTe$ contact regions to suppress Auger processes and minimize parasitic impedances,
- monolithic optical immersion microlenses were used as optical concentrators. The lenses were formed from the substrates of epitaxial layers (CdZnTe). One order gain in detectivity and two orders gains in RC time constant-limited speed of response have been obtained with GaAs hyperhemispherical immersion lenses. The single microlenses (0.5–10 mm dia) were prepared by conventional optical machining. 2D arrays have been prepared in collective way with photolithography assisted dry and wet etching techniques,
- encapsulation of absorber with wide gap material has been used in some devices to prevent surface and interface generation and recombination,
- retroreflector has been applied to enhance absorption of IR radiation,
- the heterostructures have been designed to obtain a low finesse optical resonance due to reflections at the substrate-heterostructure interfaces, internal interfaces, and the heterostructure top surface,
- these measures shield the absorber region against background thermal radiation prevent unwanted optical generation.

During the last two decades, various HOT devices that comply with the requirements of the 3DHC concept have been developed including photoconductive, photoelectromagnetic, magnetoconcentration, Dember and photovoltaic detectors [50].

The present efforts are concentrated on photovoltaic devices. They do not require electrical nor magnetic bias; shown no flicker noise. Potentially, the photovoltaic devices should achieve fundamental limits. In practice, the long wavelength photovoltaic devices operating at near room temperature show poor performance [49,50].

Since the absorption depth of long wavelength IR radiation ($\lambda > 5$ μm) is longer than the diffusion length, only a limited fraction of the photogenerated charge can contribute to the quantum efficiency. Consider an example of an uncooled 10.6 μm photodiode. The ambipolar diffusion length is less than 2 μm while the absorption depth is ≈13 μm. This reduces the quantum efficiency to ≈15% for a single pass of radiation.

Another problem is a very low resistance of the p-n junction due to a high thermal generation and ambipolar effects. As a result, the noise of parasitic device resistances and preamplifier noise may exceed the thermal generation-recombination noise. These two problems make the single-cell uncooled LWIR PV devices not usable for practical applications.

These problems have been solved through adoption of sophisticated architecture of photovoltaic detectors [49–52] based on multiple heterojunctions. An example is a device with junctions planes perpendicular to the substrate (Fig. 9). This was the first commercially available uncooled and unbiased long wavelength photovoltaic detector (1995). Such devices are characterized by large voltage

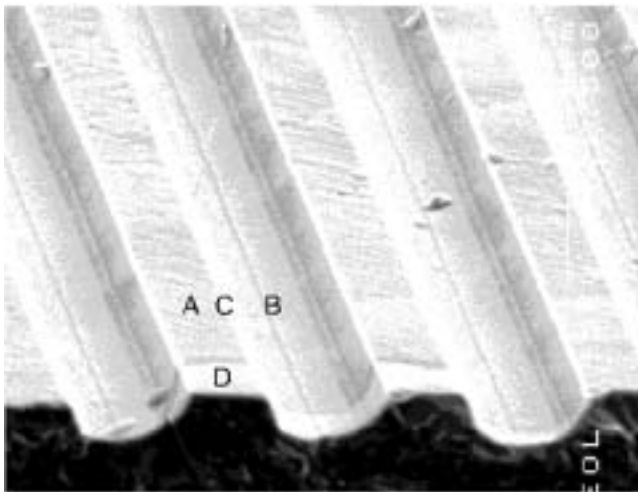

Fig. 9. SEM images of a multi-heterojunction photodetector: (a) plan view of the whole device and (b) side view of a single cell. A – mesa structure, B – trenches, C – non-metallized wall, and D – non-metallized region of the device.

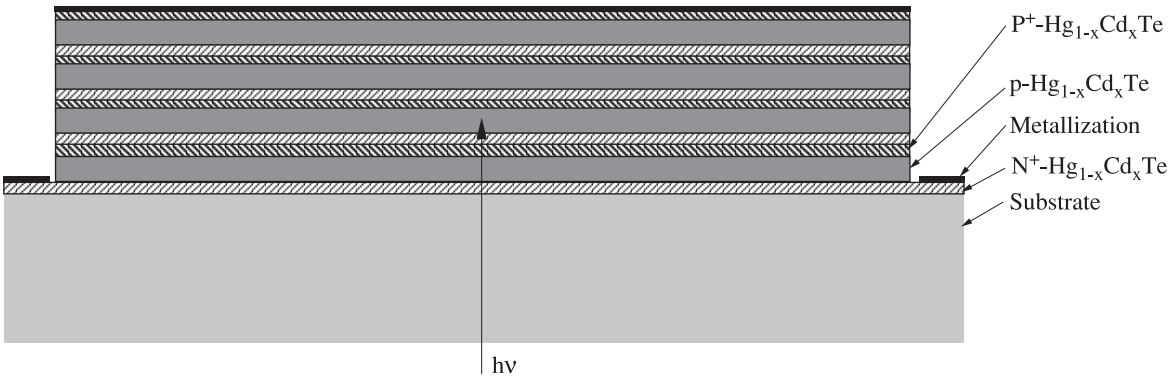

Fig. 10. Schematic cross-sections of the 4 stacked cells detector. The backside illuminated device is supplied with reflector for double pass of IR radiation.

responsivity, fast response time, but they suffer from non-uniform response across the active area and dependence of response on polarization of incident radiation.

More promising are the stacked PV cells (Fig. 10). The general design rules are:

- absorber materials optimized for the maximum ratio of the absorption coefficient to the thermal generation rate,
- thickness of the absorber region of each cell less than the ambipolar diffusion length to ensure a good collection of photogenerated carriers,
- combined thickness of all absorber regions comparable to the absorption depth of IR radiation for which the device is optimized. This ensures good use of incident photons.

Such devices are capable of achieving high quantum efficiency, large differential resistance, and fast response. The practical problem is the shortage of adjacent N^+ and P^+ regions. This can be achieved employing tunnel currents at the N^+ and P^+ interface.

2.4. Practical devices

At present, VIGO System offers photoconductive, photoelectromagnetic and photovoltaic devices optimized at any wavelength in the LWIR, MWIR and SWIR range of infrared spectrum [49,53,54]. The longest usable wavelength are 11, 13, and 15 μm for uncooled, 2- and 3-stage Peltier coolers, respectively. The formats are single elements with sizes from few μm to a few mm, linear arrays up to 120 elements, small 2D arrays.

Figure 11 shows the picture and performance of the devices. Without optical immersion MWIR photovoltaic detectors are sub-BLIP devices with performance close to the G-R limit but well designed optically immersed devices approach BLIP limit when thermoelectrically cooled with 2-stage Peltier coolers. Situation is less favourable for > 8 μm LWIR photovoltaic detectors. Despite all improvements (advanced architecture, optical immersion, Peltier cooling) they show detectivities below the BLIP limit by more than order of magnitude. Typically, the devices are used at zero bias. The attempts to use Auger suppressed non-equilibrium devices were not successful due to large $1/f$ noise extending to ≈100 MHz both in extracted photodiodes and magnetoconcentration devices [55].

The HOT devices are characterized by a very fast response. The uncooled ≈10 μm photodetectors show ≈1 ns or less response time, determined by a short recombination time. More slow are < 10 μm PC devices, especially thermoelectrically cooled. Their speed of response could be improved with heavier doping than required for optimized performance or using sweep out of minority carriers.

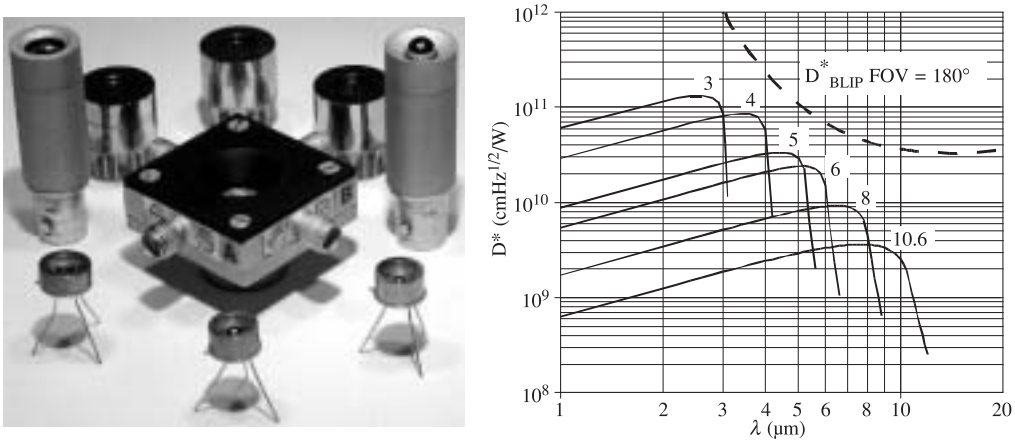

Fig. 11. Packages of uncooled and Peltier cooled detectors and spectral performance of optically immersed devices cooled with 2-stage coolers.

Fig. 12. Infrared systems with Polish HOT photodetectors developed: (a) V-20 thermal imager [54], (b) MIR 8000 FTIR spectrophotometer (Oriel Corp., USA), (c) free space optical communication system (Maxima Corp., USA), and (d) Polish "Obra" tank laser warning systems [56].

Much faster are photoelectromagnetic devices in which time constant is much shorter than the bulk recombination time due to fast diffusion of minority carriers to a high recombination velocity surface.

Lastly, the photovoltaic devices have been optimized. The RC time constant was shorten by the use of optical immersion to reduce physical area of devices. The series resistance was minimized to $\approx 1\ \Omega$ using heavily doped N^+ for base regions of the mesa structures and improved anode contact. Next, transport of photogenerated charge carriers to the contacts was accelerated by the use of thin p-type absorbers and introduction of built-in electric fields induced by suitable band gap and doping grading.

2.5. Applications of HOT detectors

The uncooled photodetectors found numerous applications. They are used mostly for industrial and scientific applications. The examples are pyrometry, thermal imaging, conventional and FTIR spectroscopy, gas analyzers, plasma physics, laser metrology, laser technology, laser microfusion experiments, free space optical communication, various CO_2 and quantum cascade laser systems. Their military applications are laser rangefinders, alerters, lidars, guidance, tracking and many other. Figure 12 shows a few examples of IR systems with the HOT photodetectors manufactured in Poland.

3. Conclusions

The development of $Hg_{1-x}Cd_xTe$ as a new semiconductor in Poland began with academic research and resulted in industrial exploitation of the material for infrared photodetectors. Polish efforts have been concentrated mostly on the uncooled long wavelength devices rather than on the mainstream of detector industry – the LN-cooled 2D arrays for thermal imaging. That has happened mostly due to the lack of adequate financing; the HOT devices did not require extreme technologies and expensive equipment.

Ways to perfect detection without cooling have been recognized and suitable technologies developed. The HOT devices corresponding to 3D heterostructure concept have been implemented with ISOVPE and MOCVD epitaxial techniques and specific processing technologies. That became the basis of low volume, fast cycle times and flexible manufacturing of the infrared detectors with affordable costs corresponding to the niche needs of the IR industry.

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ANNOUNCEMENT & CALL FOR ABSTRACTS

QWIP2006

(International Workshop on Quantum Well Infrared Photodetectors)
June 18-24, 2006
Kandy, Sri Lanka
Webpage: http://www.phy-astr.gsu.edu/qwip2006/index.htm

On behalf of the organizing committee, I am happy to announce that the 4th QWIP workshop will be held in Kandy, Sri Lanka as planned during the QWIP-2004 workshop in Canada. The topics to be covered include (but not limited to) QWIP & QDOT Physics, technology, applications, Innovative directions, engineering issues. Other competing quantum technologies, such as HgCdTe, InSb, supperlattices, and other heterojunction/ homojunction will also be considered. Please mark your calendar and plan to submit your abstracts to the workshop before January 15th 2006. Travel support for (about 10) US students and post-docs who will be presenting authors will be available. Several Tutorials on QWIP physics, technology, novel directions and Photon detection using dye-sensitized nanostructures are also planned.

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A. G. U. Perera chair	Georgia State University USA
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