INSTRUMENTS AND METHODS OF INVESTIGATION

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Cadmium mercury telluride and the new generation of photoelectronic devices

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Contents

Abstract. **This paper is a 1969 – 2002 progress report on the development of solid semiconductor solutions of cadmium-mercury tellurides (single crystals and epitaxial layers) as well as of infrared photodetectors based on them (photoresistors and photodiodes, including the array variety).**

1. Introduction

An analysis of preferences for various photosensitive materials in the design of photoelectronic devices destined for recording IR radiation shows that solid solutions of cadmium mercury tellurides $Cd_xHg_{1-x}Te$ (CMTs) have been stably ranking high for the last two decades. This is particularly true of IR imaging in the 8 – 14 μm spectral range.

Two main periods can be distinguished in the development of CMT-detector-based optoelectronics:

1970 – 1990. Gradual development of material and detector technology (photoresistor and photodiode technology) resulted in the production of a family of basic unified photodetector devices with 10, 20, 60, 120, or 180 elements (abroad, they are commonly referred to as the system of common modules). During the same period C T Elliott developed a detector with processing signal accumulation (ISA) in the element (see Section 2). The 1980s and the ensuing years saw the development and commissioning of the overwhelming majority of diversified optoelectronic equipment, which was based on these photodetectors and was intended for operation in the 8 – 14 μm terrestrial atmospheric transparency 'window.' When mass-produced, detector prices dropped by more than an order of magnitude.

1990 – 2002. On the eve of this period, a change of priorities in the field of IR imaging engineering design occurred. Research into the development of a radically new type of CMT device for new-generation IR imagers was undertaken in the USA, England, France, and Germany. Multielement photodetectors (subarrays) were employed on the basis of photodiodes of format 4×N, 6×N, etc., which were integrated with cooled microelectronics in the immediate vicinity of the sensitive elements. Their use in instrumentation with optomechanical scanning made it possible not only to increase the number of photosensitive elements by a factor of 4 – 10 for a relatively small detector size, but also to realize the operating mode of time delay and integration (TDI), with a consequential 1.5 – 2-fold rise in the detection ability of the device. Simultaneously, a start was made on the industrial manufacture of staring arrays of size 128 × 128, 256 × 256, 384 × 288, or more for IR imagers without mechanical image scanning. Similar photodetectors were developed in Russia as well.

At present, such CMT-based 'staring' and TDI arrays are commonly referred to as new-generation photoelectronic devices for IR imaging, IR direction finding, and laser ranging and communication in the IR spectral range.

By 2000, 40 years had passed since the commencement of CMT research in the Soviet Union and more than 30 years since a start was made in work on CMT and CMT-based devices at the Research Institute of Applied Physics (NIIPF) (Moscow). In 1986, a review concerned with the basic properties of cadmium mercury telluride [1] was published in the collection of articles entitled *Fizika Soedinenii* $A^{II}B^{VI}$ (*Physics of* $A^{II}B^{VI}$ *Compounds*). L N Kurbatov, a Corresponding Member of the Russian Academy of Sciences, published his papers on the CMT problem [2, 3]. Prof. N S Baryshev's monograph, which contained an extensive review of the properties and applications of narrow-gap semiconductors, appeared in 2000 [4].

My paper describes in greater detail the main stages of CMT research pursued in the defense industry, nonferrous metallurgy, and the Russian Academy of Sciences.

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2. Development of single crystals and epitaxial layers. First-generation photodetectors

Research on narrow-gap $Cd_xHg_{1-x}Te$ solid solutions commenced at NIIPF in the second half of the 1960s. Considered to be the 'narrowest-gap' semiconductor compounds among those actively studied at that time were indium antimonide ($E_g \cong 0.23$ eV, $T = 77$ K), lead selenide ($E_g \cong 0.29$ eV, $T = 300$ K), and indium arsenide ($E_g \cong 0.41$ eV, $T = 77$ K). Intensive research on the compounds of the Group III and Group IV elements of the Periodic system was underway at that time. Among these investigations are, first and foremost, the works of A R Regel' and N A Goryunova (USSR), as well as of H Welker (Germany) on indium antimonide. In 1952, Welker showed that $A^{III}B^{V}$ compounds manifest exceptionally interesting properties, that all of them are semiconductors, and that they are intimately related to the semiconductor Group IV elements of the Periodic system. All of them exhibit photosensitivity at liquid-nitrogen temperatures in the 3–5 μm wavelength range. Subsequently, research on $A^{III}B^{V}$ compounds was successfully pursued in the Ioffe Physico-technical Institute (Leningrad) and in other institutions.

In narrow-gap semiconductors, the charge-carrier energy spectrum is strongly nonparabolic owing to the proximity of bands. In 1957, Kane's theory made its appearance [5], which provided a semiquantitative description of semiconductor band structure with the use of a **kp** perturbation model and enabled the formulation of the charge-carrier dispersion law. This made it possible to provide a satisfactory explanation of quite a number of transfer phenomena in indium antimonide and other $A^{III}B^{V}$ compounds with a relatively narrow energy gap.

Late in the 1950s, a start was made on the thorough study of the $A^{III}B^{V}$ compounds. The study was made of CdS–CdSe, ZnTe–CdTe, HgS–HgSe–HgTe, and other solid solutions.

Lastly, W D Lawson [6] of the Royal Radar Establishment (England) in 1959 and A D Shneider [7] of the L'vov Pedagogical Institute (USSR) in 1960 published the first two papers concerned with the investigation of the CdTe–HgTe system. Despite the fact that cadmium telluride and mercury telluride had been well known by that time, HgTe being recognized as a semiconductor with a very narrow energy gap (~ 0.02 eV for $T = 4.2$ K), the emergence of solid solutions in this system was not evident. From the above papers it followed that both compounds possess infinite mutual solubility and form a continuous series of solid solutions with a smoothly varying width of the energy gap. Even at that time both papers emphasized that CdHgTe was potentially a candidate for IR radiation detection over a wide range. Indeed, by varying the composition x of the $Cd_xHg_{1-x}Te$ solid solution between 0.2 and 0.5, it was possible to obtain a material suitable for IR radiation detection in all three terrestrial transparency 'windows,' namely 1.5–2.5, 3–5, and 8–14 μm. It is generally agreed that the publication dates of these papers are the 'birthdays' of one of the most important semiconductor materials, whose emergence resulted in a genuine revolution in photo- and optoelectronics.

The investigations were vigorously continued in England and especially in France and the USA. The Vietnam war experience convinced the military and political leaders of these countries of the necessity to pursue IR imaging research, first and foremost in the so-called 'far' IR spectral range (8–14 μm). This is precisely the range wherein lies the peak of the spectral emissive power of camouflaged military equipment, objectives, enemy manpower, etc.

In the late 1960s, CMT ingots were produced abroad, which were suitable for manufacturing photodetectors. By that time there was information that multielement photoresistors had been fabricated by Honeywell in the USA and by Mullard in England. In France, preference had been given to photodiodes. There, C Verie [8] had obtained CMT photodiodes with a detectivity $D^*_{\lambda\,\max} = (1-5)\times 10^9$ cm Hz$^{1/2}$ W^{-1} by 1967.

M Raudot of the French National Center for Scientific Research (CNRS) and H Raudot, his spouse, can be considered the pioneers of CMT research in France. M Raudot's monograph was published in Paris in 1965, translated and published in the USSR in 1971 [9]. It described some CMT properties and contained some information, or rather warnings, on the complexity and delicacy of CMT fabrication procedures. Also emphasized was the requirement of low foreign impurity content in the initial Cd, Hg, and Te.

In the USSR, the first work on CMT technology was launched in the Scientific-Research Institute of Applied Physics with the active support of the Institute supervisors (Yu N Solov'ev, L N Kurbatov) in January of 1969 (the Moda Project, with L A Bovina as the scientific project leader). Employed in this work was F F Kharakhorin's Laboratory in the department supervised by E V Susov at the moment the project was formulated. A short time later, Professor V I Stafeev headed the department, L A Bovina's Group was elevated into a laboratory, and the development of CMT-based detectors was pursued in G E Popovyan's group, where a start was soon made on the work on detectors employing the material grown there.

At the time of the commencement of CMT research at NIIPF, rather little had been learned about the technology and properties of the material, to say nothing of any integrated picture of the physical phenomena in CMT-based structures and devices. Even the phase diagram of the Cd–Hg–Te system had not been accurately determined. However, some 'obnoxious' features of CMT growth technology were already known:

— cadmium, mercury, and tellurium possess rather high vapor pressures above the melt, which may be responsible for significant departures from stoichiometry; in the calculation of equilibrium in the solid–liquid–vapor system, which permits one to obtain a material with a nearly stoichiometric composition, account should be taken of not only the mercury pressure, but of the cadmium pressure as well, which is extremely difficult to do;

— the large difference in the densities of the components in the Cd–Hg–Te system should lead to gravitational segregation of mercury telluride relative to cadmium telluride and hence to a strong ingot nonuniformity in composition.

The work on the Moda Project began with designing and fabricating the equipment for growing single crystals. The Bridgman technique, which had been used to advantage in growing other semiconductors, was adopted as a basis. In this case it was clear that obtaining a relatively narrow composition range $x = 0.18-0.21$, which was needed for detectors in the 8–14 μm spectral range, required that the temperature in the melt region should be about 800 °C; the temperature of the 'cold' point, which determines the equilibrium mercury vapor pressure in the system, is about 600 °C (the pressure itself exceeds 12 atm at this temperature). Under these conditions, a departure in the growth regime of only 1 °C resulted in pressure variations of 0.2 atm, which was sufficient to cause a significant change in composition. All these regimes had to be realized in quartz ampules under high-purity conditions. This made the procedure not only an extremely delicate task, but also to an extent a dangerous one, due to the possibility of explosion of mercury-bearing ampules. Such equipment was not available in the USSR, and the first growth facilities were designed and manufactured at NIIPF entirely with its own effort (Fig. 1).

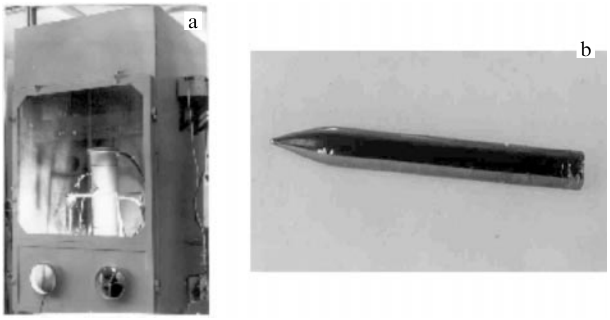

Figure 1. (a) Unit for growing CMT using the Bridgman technique manufactured at NIIPF in 1969. (b) One of the first single-crystal CMT ingots grown at the NIIPF in 1969 (L A Bovina, V P Meshcheryakova, T P Bogdanova, L V Stepanyuk, E A Sychevskaya, V F Sokolov, et al.).

The first ingots of the single-crystal material were already synthesized in late 1969, and it was possible to cut small plates of the necessary composition out of them. However, inhomogeneities were sometimes encountered even within these 'bits,' giving rise to shifts of photosensitivity peaks in a range up to several micrometers. The first step was nevertheless taken. The group headed by G E Popovyan fabricated the first single-element photoresistors for a wavelength of 10.6 μm with a photosensitive area measuring 1 × 1 mm and with $D^*_{\lambda\,\max} = 10^8$ cm Hz$^{1/2}$ W^{-1} (the Azot Project). Their production technology resembled the technology then employed in the development of indium antimonide detectors with a 'mesa' contact (Fig. 2). These devices would be immediately delivered to different organizations and gained widespread acceptance in optoelectronic instrument making to record radiation with a wavelength of about 10 μm.

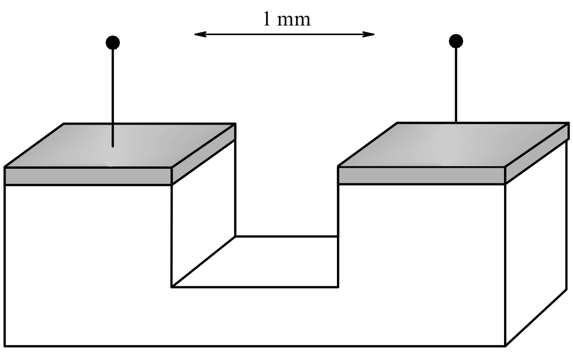

Figure 2. A mesa structure of an Azot single-area CMT photoresistor with elevated contacts (NIIPF, 1970).

In the USSR, the recognition of the promise of CMT research was by no means immediate. In IR imaging and IR direction finding, efforts were underway to design optoelectronic instruments for the near and medium IR spectral ranges employing PbS, PbSe, InSb, and other materials. The 8 – 14 μm spectral range was dominated primarily by mercury-doped germanium and boron-, gallium-, and arsenic-doped silicon. Photodetectors whose sensitivity threshold corresponds to the theoretical limit are said to operate in the mode of limitation by background-photon-number fluctuations (the FL mode). In this mode, which is referred to as the Background Limited Infrared Photodetector (BLIP) mode in English terminology, it is only the random nature of photon emission that limits the minimal power detectable by a given detector. Although Ge:Hg-based detectors can function at the temperature of liquid nitrogen, having in this case a long-wavelength detection limit of ~ 9.6 μm, the highest temperature whereby the BLIP mode can be realized for them is equal to 35 K. For doped silicon detectors this temperature is 20 – 30 K. That is why photodetectors based on extrinsic photoconductivity, which rely on rather bulky and power-consuming deeply cooled systems, could be accommodated only on heavy carriers in aircraft and the navy. Furthermore, the 1960s in the USSR was a period of rapid progress in microwave engineering and it was assumed that the majority of problems could be solved by radar techniques, with only an auxiliary part being assigned to IR imaging.

In the late 1960s, a creative body of talented physicists and technologists began to form at NIIPF. They made an invaluable contribution to the formation of this new field of semiconductor physics — narrow-gap solid solutions (L A Bovina, G E Popovyan, V P Meshcheryakova, E A Sychevskaya, T P Bogdanova, L V Stepanyuk, V F Sokolov, V S Makarevskiĭ, E S Banin, V G Grigor'ev, V E Lozhnikov, K M Kulikov, N Kh Sekamova, and many others).

In 1970, in connection with the work on high-power gas-dynamic CO_2 lasers utilizing solid fuel, there arose an acute demand for broadband 10.6-μm photodetectors for optical ranging of fast-moving objects. Development was tasked to the Strela Moscow Design Bureau (Academician B V Bunkin). In this case, the detectors were to record the laser radiation reflected from a target at a power level of 10^{-18} – 10^{-19} W Hz^{-1} at frequencies of 0.5 – 1.0 GHz. Somewhat later, a problem was raised on the initiative of the Research Institute of Space Instrument Building, which consisted in the development of detectors intended for laser data transmission from remote space objects in the frequency band up to 600 MHz and about the same requirements on threshold power.

The n-type CMT photoresistors, which were already being developed at NIIPF at that time, were unfit for this purpose. Their speed of response was primarily limited by the longest lifetime of photoexcited nonequilibrium charge carriers or the carrier lifetime in the extraction mode. By contrast, the critical parameters that define the speed of response of p – n-junction photodiodes are mostly the diffusion or drift time τ_d of the photocarriers from the place of their production to the p – n-junction, the flight time τ_t through the space-charge layer, and the charging time constant of the p – n junction capacitance τ_{RC}. Part of these parameters can be controlled by technological production procedures and the photodiode geometry. From narrow-gap CMT solid solutions with a low dielectric constant $\varepsilon \cong 12$ and a high electron mobility $\mu_n > 10^5$ cm^2 V^{-1} s^{-1}, one would expect to obtain detectors with a speed of response ranging into hundreds of megahertz and higher.

During the period 1972 – 1976, a start was made on the first research-and-development works to develop fast-response photodiodes for the detection of CO_2-laser radiation (the Dnepr-1, Dnepr-2, Dnepr, Spartak-1, and Semafor research works, the 'Dunai' development work; scientific supervisor: V I Stafeev). This work proceeded fast. Experts from different research organizations of the Soviet Union gradually joined in the work [State Research Institute for the Rare-Metals Industry (GIREDMET) — É P Bochkarev, A V Elyutin, M G Mil'vidskiĭ, E A Rashevskaya, O V Pelevin; State Institute of Applied Optics (GIPO) — A P Cherkasov, N S Baryshev, I S Aver'yanov; Ioffe Physicotechnical Institute (FTI) — V I Ivanov-Omskiĭ, V K Ogorodnikov, K P Smekalova; P N Lebedev Physical Institute of the USSR Academy of Sciences (FIAN) — A P Shotov, E A Kalyuzhnaya; L'vov State University — V G Savitskiĭ, M V Pashkovskiĭ; Institute of Semiconductor Physics, Academy of Sciences of Ukrainian SSR (IPAN) — E A Sal'kov; M V Lomonosov Moscow State University (MGU) — N B Brandt, Ya G Ponomarev; Tomsk State University — A V Voĭtsekhovskiĭ; and many others].

The early 1970s already saw the production of the first domestic single- and four-element CMT photodiodes made on the basis of the material grown at NIIPF. At that time the technology permitted the making of detectors with a sensitive area measuring only 200 – 400 μm on a side (Fig. 3). Special techniques employing optical heterodyning in the IR spectral range were introduced for their investigation (K M Kulikov, V E Lozhnikov). This technique, which is used for the extraction of the useful signal and the suppression of the interference in radar systems, offered several advantages in comparison with direct photodetection: a high sensitivity, a good frequency selectivity, a well-defined directional property, and the capacity to measure the velocity from the Doppler frequency shift, which was crucially important for the predetermined fields of application of these photodetectors. The measured heterodyne threshold for the resultant photodiodes was 6×10^{-20} W Hz^{-1} in the band ranging up to 1 GHz and 4×10^{-20} W Hz^{-1} in the band up to 600 MHz. To conduct these investigations, a unique electrooptical hot-electron modulator with a response time of the order of 10^{-10} s (L E Vorob'ev) was developed at the Leningrad Polytechnical Institute. The limit defined by the quantum noise of an 'ideal' photodiode for a wavelength of 10.6 μm is approximately equal to 2×10^{-20} W Hz^{-1}. Therefore, the detectors developed realized in fact a single-photon detection mode for IR radiation.

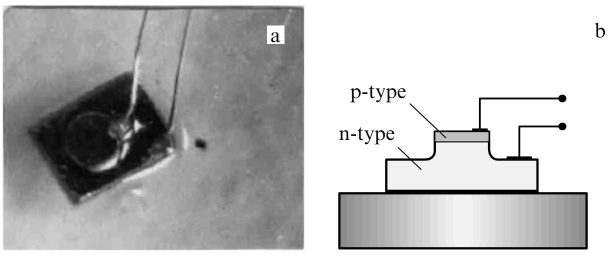

Figure 3. (a) A Dunaĭ single-element broadband photodiode (NIIPF, 1976) with photosensitive element measuring 350 × 350 μm and (b) a mesa structure of a Dnepr-1 single-element photodiode (NIIPF, 1972) with a photosensitive element measuring 300 × 300 μm.

Intensive work on the material was simultaneously underway. An extensive complex study was made on the nature of internal defects, galvanomagnetic and photoelectric effects, structural perfection, diffusion kinetics, and other effects. Many of the findings of these investigations were pioneering in nature. For instance, the dependences of diffusion coefficients for Hg, Cd, and other atoms on the temperature and crystal characteristics were obtained for the first time in the world [10 – 12]. The foundations were elaborated for p – n-junction production techniques, two of which have gained the widest acceptance: the method of controlling stoichiometry by the diffusion of mercury and cadmium atoms from the vapor phase and the method of indium diffusion from a mercury – indium solution [13]. Equipment was designed and a method was introduced for growing graded epitaxial CMT layers by vaporizing a HgTe source with subsequent vapor transfer onto a CdTe substrate and the interdiffusion of these compounds [14, 15]. The results of this work, which marked the beginning of the investigations of physicochemical CMT properties, were later taken advantage of in the development of industrial CMT single-crystal technology at GIREDMET and at the Factory of Pure Metals (ZChM, Svetlovodsk, Ukraine).

By 1970, in connection with a rapidly increasing flow of papers on CMT-based detectors, it became evident that the efforts of NIIPF alone to grow crystals and epitaxial films were clearly insufficient. It was necessary to develop an industrial technology and organize CMT production on a commercial scale. The first attempt to charge the Ust'-Kamenogorskiĭ Polymetal Group of Enterprises with growing single crystals undertaken in 1970 – 1972 did not meet with success. They had no experience in working with ultrapure and mercury-bearing materials. In March of 1973, after a meeting of the Ministers of Defense and Non-Ferrous Metallurgy, S A Zverev and P F Lomako, GIREDMET and ZChM were charged with the solution of the problem of industrial technology and CMT production. The task of scientific supervision of these works was entrusted to NIIPF, where the Pamir and Nurek Projects were launched (the development of technology and the organization of the production of pilot batches of single crystals and epitaxial layers of CMT; scientific supervisor: V I Stafeev). The results obtained at NIIPF, GIPO, Ioffe FTI, and L'vov State University were adopted as a basis for an industrially suited technology standard. Beginning in 1974, GIREDMET and NIIPF were engaged in technology transference to ZChM. However, it took 5 – 7 years for the factory to master the production of sufficient amount of material suited for the development and fabrication of photoresistors with 10 – 130 elements [n-type material with a density of majority charge carriers $n = (2-5) \times 10^{14}$ cm^{-3}].

CMT production relied on a complex multistage technology. It involved a deep purification of the initial Cd, Hg, and Te; the synthesis of HgTe and CdTe binary compounds; and the production of CdHgTe polycrystals with subsequent solid-state recrystallization of the ingots at a temperature of 750 ± 1 °C for growing single crystals of required composition. In addition to solid-state recrystallization, two more growth techniques were successfully developed: the method of directional crystallization in a region with a temperature gradient and a modified Bridgman technique, whereby the crystal growth is effected at a lower temperature from the two-phase mixture (melt + solid phase) using a continuous replenishment of the melt with the solid phase having a higher content of cadmium telluride. When the ampule in the crystal-growth apparatus moves with a velocity of $0.1-1$ mm h^{-1}, the ingot synthesis lasts from several weeks to several months. Unique equipment for growing CMT was developed by designers at GIREDMET and made in the pilot works. As a rule, immediately after synthesis the single crystals contained a great number of structural defects related both to simple mercury vacancies with a low ionization energy and to complex vacancies involving displacements of the neighboring tellurium atoms. This radically distinguishes CMT from the majority of semiconductors: not only do impurity atoms prove to be electrically active in this case, but the intrinsic point defects of the crystal lattice are as well. To obtain a low electron density in n-type CMT, the material samples should therefore be subjected to a slow high-temperature annealing in saturated mercury or mercury – cadmium vapor with a strict maintenance of the regimes for several hundred hours. All this made this material extremely expensive and impelled researchers to searching for alternative solid solutions (for instance, Pb – Sn – Te, Pb – Sn – Se, etc.). Nevertheless, by the mid-80s, CMT became firmly established as the world's principal material of IR photoelectronics, leaving far behind in amount of sale all other semiconductor photosensitive materials. A large contribution to the mastering of CMT technology at ZChM was made not only by GIREDMET and NIIPF, but also by the selfless labor of the factory personnel (A M Tuzovskiĭ, Yu N Gavrilyuk, V K Ergakov, K R Kurbanov, A M Raskevich). As a result, by the mid-80s the problem of industrial production of bulk n-type single crystals was successfully solved in the USSR.

Despite remarkable progress in the development of industrial photoresistor-material technology, the problem of production of CMT suited for multielement photodiodes was still acute. Early in the development, it was assumed that the p-type single-crystal technology was much simpler than that for the n-type single crystals employed in the photoresistors because the carrier density in the material employed in the photodiodes must be considerably higher ($10^{16}-10^{17}$ cm^{-3}). However, investigations revealed that the photodiode-material technology was in reality significantly more complicated, for the requirements on structural perfection were far more stringent. The physicochemical properties of the Cd – Hg – Te system were, quite to the contrary, not very conductive to the fabrication of a material with a perfect crystallinity: the system is prone to constitutional supercooling and the homogeneity range of the solid solution is strongly shifted to the tellurium side, resulting in various inclusions, low-angle boundaries, and other defects (Fig. 4).

The fabrication procedure of p-type single crystals employed at ZChM comprised two main stages: the fabrication of n-type CMT with a free-electron density of $\sim 10^{14}$ cm^{-3}, which was indicative of rather high structural perfection, and the subsequent annealing of selected plates at a low mercury vapor pressure to obtain a material with a mercury vacancy density of $(0.8-1.0)\times10^{16}$ cm^{-3}. This called for thorough studies into the nature of structural imperfection and the ways to reveal it. Nevertheless, the problem of photodiode-material growth had never been solved: the material did not possess the structural perfection required for the production of multielement photodiodes. The presence of numerous structural defects was responsible for the leakage through the p – n junction and the associated lowering of the magnitude of R_0A (R_0 is the differential resistance and A the photodiode area) or even to the complete p – n-junction shunting.

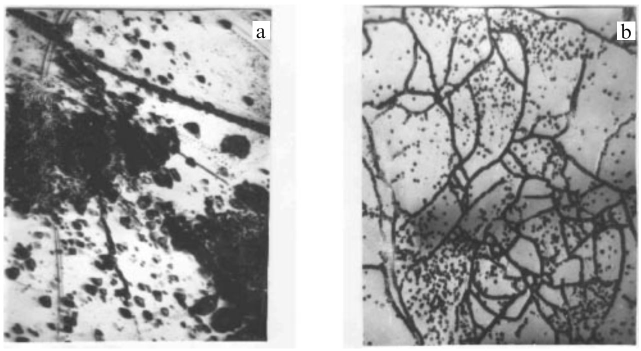

Figure 4. Structural imperfections in CMT: (a) second-phase tellurium-enriched inclusions in p-type CMT; and (b) low-angle boundaries in a p-type CMT sample.

However, attempts to fabricate multielement photodiodes persisted despite an extremely low fractional yield. In particular, the first 10-element photodiodes with a sensitive area measuring 300×300 μm intended for laser detection and ranging at a wavelength of 10.6 μm (the Ladoga Project) were produced at NIIPF in 1980. Not only were the photodiodes, which had the form of 10-element mesa structures (Fig. 5), produced in the framework of this work, but a start was also made on the development of the foundations of planar photodiode technology: n^+-p junctions were produced by ion implantation (Ga, Al, or In ions) or by diffusion from a metal layer predeposited on the sample surface. The configurations of the photosensitive element and the contact regions were produced by photolithographic techniques (Figs 5 and 6).

The average value of the heterodyne threshold for these photodiodes was equal to $\sim 5.5\times10^{-19}$ W Hz^{-1} at a modulation frequency of 100 MHz.

At the same time, the first investigation was made of the high-frequency properties of multielement photoresistors, including p-CMT-based ones. The speed of response of the latter is normally limited not by the bulk lifetime of nonequilibrium charge carriers ($10^{-6}-10^{-7}$ s), but by the time of their ambipolar drift to the contacts $t_a = L/\mu_a U_{ph}$ (L is the

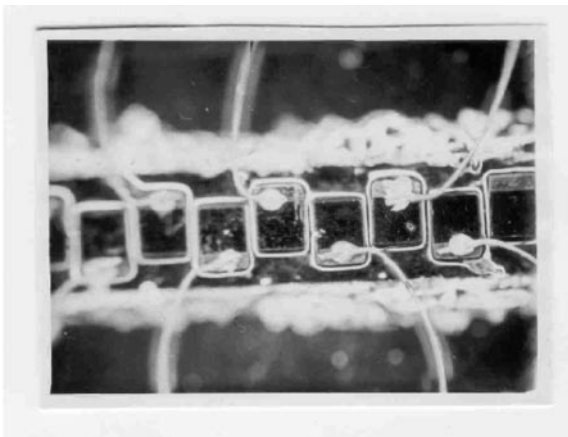

Figure 5. Fragment of a Ladoga 10-element photodiode mesa structure (NIIPF, 1980). The photosensitive element measures 300×300 μm.

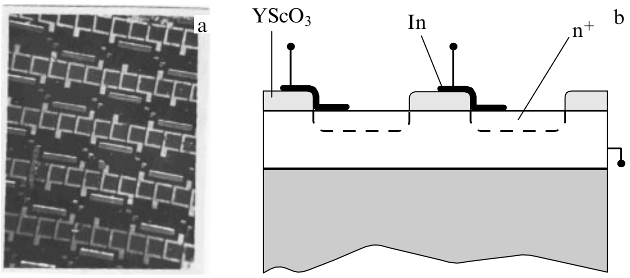

Figure 6. (a) Fragment of a Ladoga planar 10-element photodiode mesa structure (NIIPF, 1980); and (b) a Ladoga planar photodiode structure.

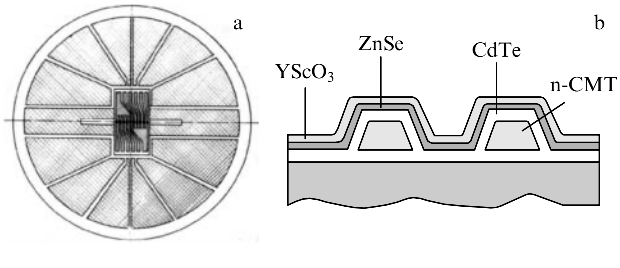

Figure 7. CMT-based photoresistors made using planar technology: (a) a Nevesomost'-10 10-element linear array (50 × 50 μm) (NIIPF, 1979); and (b) the structure of photosensitive elements with a three-layer protective coating.

contact spacing, U_{ph} is the photoresistor bias voltage, and $\mu_{\mathrm{a}} = \mu_{\mathrm{n}}\mu_{\mathrm{p}}(n-p)(n\mu_{\mathrm{n}} + p\mu_{\mathrm{p}})^{-1}$ is the ambipolar mobility of the nonequilibrium carriers). For a p-CMT photoresistor with $L \cong 0.3$ mm, $\mu_{\mathrm{n}} \sim 10^5$ cm^2 V^{-1} s^{-1}, $\mu_{\mathrm{p}} \sim 10^2$ cm^2 V^{-1} s^{-1}, $p \gg n$, and $p\mu_{\mathrm{p}} \gg n\mu_{\mathrm{n}}$, the magnitude of t_{a} proves to be on the order of 10^{-8} s. Therefore, by employing p-type CMT as the material for photoresistor fabrication, it was possible to significantly improve their speed of response. A threshold of $(0.8-1.9) \times 10^{-19}$ W Hz^{-1} was realized in the heterodyne mode for a modulation frequency of 60 MHz. Recently it was shown that a heterodyne threshold of $(4-6) \times 10^{-19}$ W Hz^{-1} in a frequency band ranging up to 40 MHz can be reached for n-type CMT photoresistors with a photosensitive area measuring 35×35 μm and a spectral density of the emf of the preamplifier noise $\leqslant 1$ nV Hz$^{-1/2}$ [16].

Late in the 1970s, the problem of stability of the parameters of CMT-based devices became urgent. The binding energy of mercury atoms in the crystal lattice of CMT is lower than for cadmium and tellurium. That is why even a not-too-long heating to temperatures above 80 °C can result in the growth of mercury-vacancy density and the degradation of the parameters of photoresistors fabricated from n-type material ($n \cong 10^{14}$ cm^{-3}) [17]. Devices made of p-type CMT ($p \cong 10^{16}$ cm^{-3}) are less sensitive to elevated temperatures. At first, the parameters of devices, including the foreign ones, were observed to change even at room temperature. However, it developed that this was due not to CMT properties, but to mistakes in the technology of assembling the sensitive elements in the casing of the device. Indeed, the sensitive element is located in the coolest region, and foreign impurities that reside within the casing volume are primarily adsorbed into the sensitive element. By eliminating the sources of such residual impurities from device structures (elements based on organic materials, soldering procedures with the use of acidic fluxes, etc.) it was possible to solve this problem. However, the stability problem was completely solved only in the first half of the 1980s after the development of a technology that provided passivation and reliable protection of the surface of the sensitive elements. This became possible after taking drastic measures to provide the factory with state-of-the-art technological equipment, which was started by P V Finogenov, the Minister of Defense Industry, and V I Kreopalov, the Director of the institute, in the late 1970s. This made it possible to commence the development of modern planar technology of small-dimension multielement photodetectors.

Figure 7 shows the structure of a planar photodiode with a multilayer passivation, antireflection, and protective coating (M S Nikitin, L V Kiseleva) [18]. It was not long before Bovina and Nikitin [19] developed a method for the electrochemical passivation of a photoresistor surface by the CMT's own oxides, which were complex oxygen-bearing compounds of the components of the ternary system sich as TeO_2, (Cd,Hg)TeO_3, (Cd,Hg)TeO_5, and other materials. This provided low surface recombination rates, while the additional protection by insulators such as ZnSe and $YScO_3$ ensured retention of the parameters of device structures.

Like the material itself, the material-based device structures proved to be extremely interesting from a physical point of view. This is particularly true of structures with p–n junctions or barriers of another nature in p-type CMT.

In particular, the year 1974 saw the first experimental discovery of a new effect of injection heat transfer in diodes made on the basis of epitaxial CMT layers, which was quite unusual for thermoelectricity [20]. In a forward-biased p–n junction, the minority carriers injected from a contact do not recombine in the volume when the diffusion length L is long enough (the L_{n} value ranges into tens of micrometers in CMT with a high electron mobility and a long lifetime), but escape to the opposite contact with the absorption of crystal lattice energy. As this takes place, the p–n junction region cools down. The low thermal conductivity of CMT ($\chi \sim 0.4$ W cm^{-1} K^{-1}) hinders the reverse heat flux. CMT thereby combines in a favorable manner the material parameters required for injection cooling, whereby a forward current through the p–n junction may be associated with a lowering of the diode temperature. Even for $T = 77$ K the experimentally recorded temperature drop was equal to 5 K. This is impossible for traditional thermoelectricity relying on the classical Peltier effect. A series of investigations into thermoelectric effects in narrow-gap CMT-based diodes revealed that in the future it would be possible in principle to produce 'self-cooling' matrices for the IR range.

The investigations of the band structure and the properties of charge carrier transfer in the new semiconductor compound were required in the development of technology and metrics of the material and material-based device structures. Already in 1976, a group headed by V P Ponomarenko was established at NIIPF to investigate galvanomagnetic, photoelectric, and thermoelectric effects, and it also oversaw cooperation issues with GIREDMET and ZChM concerning the introduction of CMT technology (D V Sobolev, N A Aristova, E A Zakharova, Yu N Savchenko, V D Vershinin). The investigations of p-type CMT at helium temperatures in weak and strong magnetic fields revealed several unusual properties of the narrow-gap compounds. In particular, two sorts of charge carriers of opposite sign were discovered in the conduction band at temperatures of 4.2–10 K [21, 22]. A model of an impurity acceptor band overlapping with the conduction band at low temperatures was put forward as an explanation. It is formed by acceptor levels split-off from the valence band that find themselves in the continuum of states of the conduction band of p-type CMT. Because of a different symmetry, the acceptor terms do not mix with the states of the conduction band and at some density ($N_a \cong 10^{17}$ cm^{-3}) are split into a band which admits hole conduction. Research at a strong hydrostatic compression and ultralow temperatures conducted at Moscow University under N B Brandt's supervision enabled the determination of the main parameters of this band (the density of states and the mobility and density of 'impurity' holes) [23]. More recently, the same properties were discovered for galvanomagnetic and thermoelectric effects in epitaxial CMT layers [24, 25]. Lastly, in 1979 it was possible to observe the impurity band in CMT directly in the investigation of absorption and photoconductivity in the ultrafar IR spectral range at photon energies $10 < \hbar\nu < 60$ meV performed by L D Saginov via high-resolution Fourier spectroscopy [26]. This finally allowed the interpretation from a unified standpoint of the whole complex of kinetic effects in narrow-gap, zero-gap, and semimetal compounds of CMT solid solutions.

The history of the development of photoresistors and photodiodes, on which NIIPF focused its efforts, largely replicated the successes and failures that accompanied the development of the starting CMT material. The first detectors with a sensitive area measuring 100–300 μm on a side were still possible to fabricate with the use of mechanical or electric-spark cutting or the simplest photolithography. That was the way used for developing Krylo, Sekunda, Vesna, and Osen' few-element photoresistors (E V Susov), a Nevesomost'-10 10-element photoresistor, Ladoga 10-element fast-response photodiodes (L A Bovina, 1979–1980), and other devices. Developed in 1980–1985 were Agava-FP 50-element photoresistors with sensitive elements measuring 50×50 μm (L A Bovina; the designer-in-chief of the instrumentation made on the basis of this detector was N F Koshchavtsev). A Lavr 200-element photoresistor (L A Bovina) with a sensitive element measuring ~ 100 μm was assembled of separate units selected on the principle that the characteristics of the elements contained in them should be most uniform. The development of planar technology of production of small-dimension detectors, where the 'chips' of multielement devices are simultaneously produced in a great number on a common CMT plate, entailed toughening the requirements on the uniformity of parameters of the initial material. In the second half of the 1980s, a highly uniform n-type CMT became available from ZChM, which made it possible to develop Nevesomost'-64 64-element photoresistors (S A Popov, O V Smolin, 1983–1987), Archa-F 128-element photoresistors (S A Popov, V V Korolev, 1983–1991), and other devices. Therefore, multielement photoresistors for the 8–14 μm spectral range, which were similar to the well-known foreign system of Common Modules, were developed successfully in the USSR by the early 1990s.

In 1982, a start was made on investigations to create detectors with internal signal accumulation in the element (of the SPRITE type) [27]. In its simplest form, the photosensitive element of this device constitutes a CMT strip ($700 \times 70 \times 10$ μm) with three ohmic contacts, two of which (the current ones, at the opposite ends of the strip) fulfil the function of applying bias (as in traditional photoresistors) while the third (the one near the current contact) is a probe for the readout of a signal. When an area on the strip is illuminated with an optical system, which forms a light spot ordinarily measuring 40–50 μm, an electron–hole gas packet forms in the strip, which drifts along the strip with an ambipolar velocity under the action of the applied field (for CMT, this velocity corresponds to that of low-mobility holes). On reaching the opposite end, this packet will change the resistance of the section of the material between the probe and the contact, which is perceived as the photosignal. In an IR imager with an optomechanical image scan, the velocity of light spot transference along the strip should be selected in such a way as to correspond to the drift velocity of the electron–hole gas packet. Therein lies the mechanism of photosignal accumulation employed by Elliott in the SPRITE (Signal Processing In The Element) photodetector. Such photodetectors make it possible to obtain a significant gain in the signal-to-noise ratio in comparison with conventional photoresistors. The drawbacks to these photodetectors are significant bias currents, which are responsible for a large heat release in the sensitive elements, and the necessity of using high-speed scanners and resorting to CMT with a lifetime of nonequilibrium charge carriers exceeding 2 μs.

The first work on such devices (the Integrator Research Work) was initiated jointly by NIIPF and the Geofizika Central Design Bureau. By 1983, the first 8-element detectors (Fig. 8) were fabricated, which possessed a detectivity of $(2-5) \times 10^{10}$ cm Hz$^{1/2}$ W^{-1} (L A Bovina). The relatively low values of $D^*_{\lambda\,\max}$ were attributed to the absence of CMT material with the required lifetime (> 2 μs). The principal factors which influenced the device operation were nevertheless investigated to allow the formulation of requirements for the material, the design, the scanning device, etc. Already in 1985 it was possible to realize the values $D^*_{\lambda_{\max}} = (1.5-2.5) \times 10^{11}$ cm Hz$^{1/2}$ W^{-1} (the Senezh Research Work; scientific supervisor: G E Popovyan). The technology of producing the sensitive elements is very close to that employed for multielement photoresistors, with the difference that, in lieu of liquid etching, advantage was taken of the technology of 'dry' etching in an argon plasma to fabricate small-dimension (on the order of 12–14 μm) readout con-

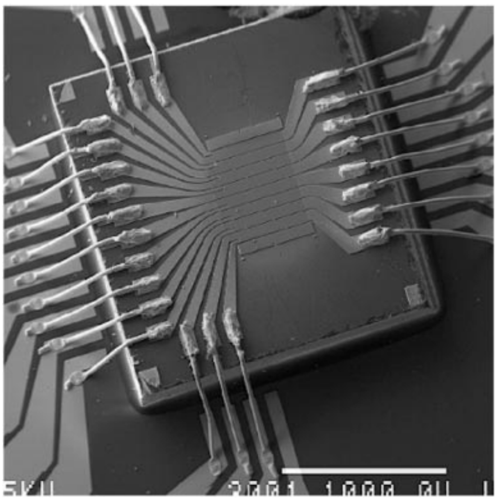

Figure 8. Photodetector with internal signal accumulation in an element (NIIPF, 1985).

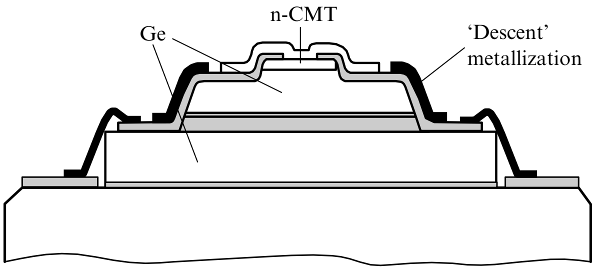

Figure 9. Structure of the sensitive elements of a multielement planar photoresistor fabricated using the 'descent' technology (NIIPF, 1999).

tacts. By the early 1990s, several types of photodetectors with internal integration were developed at NIIPF, which were supplied for IR imaging instrumentation designers.

The refinement of photoresistor fabrication technologies was continued at a later time as well. Figure 9 depicts the structure of a modern multielement planar photoresistor with sensitive elements measuring 35×35 μm, which was developed in the 1990s (Yu S Troshkin, G E Popovyan, et al.) [28]. In this case, unlike conventional technology where thin-wire current leads are connected to each element by hand by means of microsoldering, advantage was taken of a technology with a 'descent' of metallic strips along the side surface to the raster made of artificial sapphire. In this case, the wire leads (30 – 50 μm in diameter) can be connected to the metallic strips of the raster by automated microsoldering techniques without the hazard of damaging the sensitive element.

The parameters of many multielement photoresistors elaborated to date have already reached values close to the theoretical limit (Table 1). This became possible largely due to the remarkable progress in semiconductor materials science, the development of the theory of physical effects, and the technology of so complicated a compound as cadmium mercury telluride.

In the Soviet Union the first epitaxial CMT layers were obtained by L A Bovina in 1970 – 1973 using the procedure of isothermal epitaxy [13]. In this case, on CdTe substrates there grew a layer of the solid solution depth-graded in composition — from pure CdTe at some depth to highly HgTe-enriched at the surface. Comprehensive research was undertaken to investigate the composition, density, and mobility of electrons and holes, the energy gap width, and other parameters as functions of depth for epitaxial layers 25 – 30 μm in thickness [25, 29]. This enabled researchers to determine the optimal ways of fabricating p – n junctions in photodiodes for the 3 – 5- and 8 – 14-μm spectral ranges. More recently, the technology of epitaxial growth in a quasi-closed volume, where layer growth takes place in a nitrogen atmosphere at an excess pressure on the order of 1 atm, was elaborated in the Orion Scientific-Production Enterprise [30]. All this made it possible to develop the first photodiodes, including high-frequency ones, on the basis of epitaxial CMT structures at NIIPF already in the early 1970s. In the graded epitaxial layers produced by the technique described above, there actually are two potential barriers: one near the surface and the other, oppositely directed, in the $x \cong 0.2$ composition region. This structure allows us to design two-color photodiodes with a bias-controlled spectral characteristic (Fig. 10) [15].

In the second half of the 1980s, other scientific-research organizations in the country joined the CMT epitaxy research. At Nizhniĭ Novgorod State University, a start was made on research on an epitaxy technology involving metalloorganic compounds of cadmium, tellurium, and mercury (S N Ershov) [31]. The method of molecular beam epitaxy (V N Ovsyuk, Yu G Sidorov) evolved at the Institute of Semiconductor Physics, Siberian Division of the Russian Academy of Sciences [32].

3. Liquid-phase epitaxy of CMTs. Photodiode arrays

The situation that arose in world's opto- and photoelectronics by the mid-1980s can be characterized as follows:

— abroad, the scientific and technological production problems of IR-imaging instrumentation with 10 – 200 ele-

Table 1. Parameters of CMT photoresistors (the Orion Scientific-Production Enterprise).

Spectral range, μm	Cutoff wavelength, μm	Number of elements	Element size, μm	Detectivity, cm Hz$^{1/2}$ W^{-1}	Aperture angle	Cooling system	Preamplifier availability
8 – 14	11.5 – 12	1	100×100	$\geqslant 3 \times 10^{10}$	60°	*	+
8 – 14	11.5 – 12	2×12	50×50	$\geqslant 6 \times 10^{10}$	40°	*	
8 – 14	11.5 – 12	1×26	50×50	$\geqslant 7 \times 10^{10}$	26°	* * *	
8 – 14	11.5 – 12	2×26	50×50	4.1×10^{10} 7.5×10^{10} 9.5×10^{10}	180° 40° 20° × 10°	** ** *	
8 – 14	11.5 – 12	2×48	30×30	$\geqslant 4 \times 10^{10}$	24°	* * *	+
8 – 14	11.5 – 12	1×128	50×50	$\geqslant 3 \times 10^{10}$	60°	**	+
3 – 5	5 – 5.5	2×16	35×35	$\geqslant 3 \times 10^{10}$	90°	* * **	+
8 – 14 with internal integration	11.5 – 12	4 – 8	64×500	$\geqslant 2.6 \times 10^{11}$	60°	**	+

Note: * integral Stirling, ** differential split-Stirling, * * * Joule – Thomson choke heat microexchanger, * * ** thermoelectric cooler. In the structure of the differential cooler operating by the Stirling cycle, the heat exchanger is connected to the compressor with a flexible high-pressure pipeline; in the structure of the integral Stirling cooler, the sensitive element is placed directly on the cooled 'finger' of the compressor.

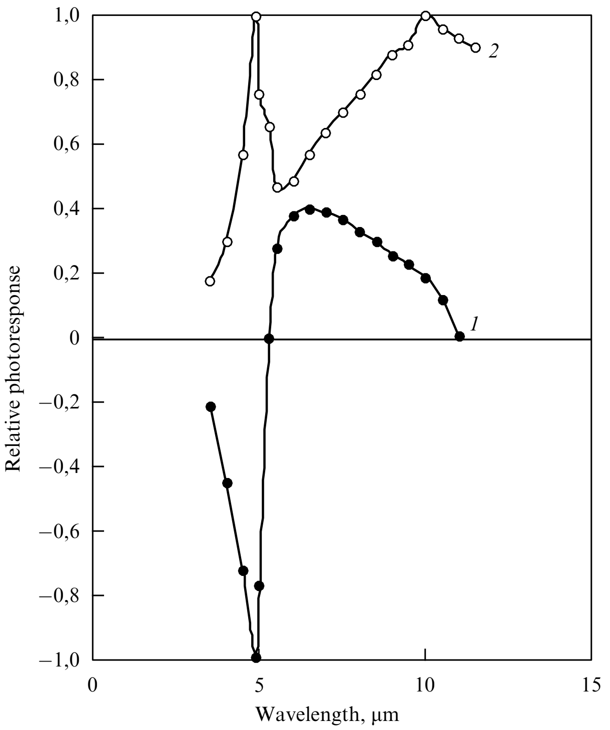

Figure 10. Spectral photoresponsivity characteristics of a photodiode on the basis of a variband epitaxial p-CMT layer obtained by the isothermal epitaxy procedure: *1*, without a bias and *2*, with a bias. There are two potential barriers in the photodiode: near the surface and in the $x \sim 0.2$ composition region.

ments had mainly been solved. Their progressive introduction into practical fire control systems and the forward-looking IR (FLIR) systems of aircraft, tanks, and helicopters made it possible to formulate quite reasonable requirements on unified modular systems, which made profitable and economically expedient the mass production of the instruments in the USA, England, France, and other countries. IR-imaging instruments in the USA and European countries exceeded 100 thousand in number. The US Department of Defense announced that it had 'saved' about 900 million dollars by purchasing 80 thousand standard detectors of the 'Common Modules' type from manufacturers instead of nonstandard devices for different kinds of arms. High-performance microcryogenic cooling systems were developed with a refrigerating capacity of 1 – 2 W. The quality of optics developed (telescope systems, detector-coupling lenses, scanning systems) was fully suited for the realization of the main tactical characteristics and specifications for instrumentation involving standard production detectors with a detectivity of $(2-5)\times 10^{10}$ cm $Hz^{1/2}$ W^{-1};

— in the USSR, by that time only photoresistor line arrays with 10 – 60 elements had come to be in demand, for which relatively compact and reliable optoelectronic equipment, like Metis and Mulat, had been developed [33]. The pilot production of these detectors was organized at the Sapfir Moscow plant, the Orion Scientific-Production Enterprise, and also at the Alfa pilot plant, which split off from the Orion Scientific-Production Enterprise in 1991. Photodetectors with more than 100 elements were produced in small numbers.

At the same time, the necessity to increase the imaging range, to radically lower the mass and size instrumentation characteristics, and to abandon mechanical scanning fostered in the late 1970s the search for new types of photodetector devices, which came to comprise two-dimensional (matrix) arrays of dimension $N \times N$, $M \times N$, $2 \times 2N$, etc. These detectors were many times more complicated than all the detectors that had been manufactured up to the beginning of this development work. It became evident that this development work called for comprehensive new materials-science and instrument research aimed primarily at the fabrication of perfect large-dimension epitaxial layers; development of modern planar technology of small-dimension photodiodes, similar to silicon technology, but taking into account the special features of CMT; surface and CMT – insulator interface investigations; development of deep-cooled silicon microelectronics with signal processing immediately in the focal plane of the detector; methods unifying photodiode and silicon microelectronic circuits; and many others. It was necessary to solve the metrology problem for detectors containing tens of thousands of photosensitive elements. Research in the field of surface-controlled devices, including CCDs and CIDs, CMT-based transistors, Schottky-barrier photodiodes, and others had to be carried out.

NIIPF was charged with the first CMT-array research in 1980. However, V I Stafeev's department was overloaded with the ongoing research and development work and was not able to place the work on a broad footing. Attempts to launch the production of cooled silicon microelectronics at the enterprises of the Ministry of Electronic Industry did not meet with success, and even attempts to come to an agreement on the technical requirements ended in failure.

In 1983, research in the field of CMT-based devices was reorganized. The department was headed by E V Susov, who was charged with bringing to completion the numerous research and development works on linear photodetector arrays. Established at the same time was the Orion Scientific-Production Enterprise and I V Ptitsyn, who was appointed Managing Director, suggested that V I Stafeev should continue multielement and matrix photodiode research in the Scientific-Research Institute for Electron and Ion Optics (NIIEIO) — an institute which also became part of the enterprise. A new engineering and laboratory building was being put into commission, which I V Ptitsyn wanted to employ for the promotion of the new promising line of research. Fourteen co-workers (L A Bovina, V P Ponomarenko, M V Sednev, T F Terekhovich, et al.) moved to NIIEIO together with V I Stafeev to form the first team of developers who commenced the new line of research involving CMT-based array photodetectors. In 1985, V T Khryapov was appointed the Managing Director of the Orion Scientific-Production Enterprise, and V I Stafeev's department became a part of a new division headed by V N Severtsev, which also contained materials science and silicon technology departments. In 1986, V P Ponomarenko was appointed Head of Division. He headed the division until 1988, when he was appointed First Deputy Science General Director in charge of scientific research. In a relatively short period, new building areas were put into service and a significant amount of state-of-the-art technological and research equipment was obtained to boost the matrix line of research. After 1988, V I Stafeev was charged with supervision of the matrix CMT photodetector division and the development of cooled silicon multiplexers commenced in the division supervised by A A Timofeev. In 1998 the two divisions were united to form a scientific-research microphotoelectronics center supervised by L D Saginov. The CMT photoresistor development line was supervised by S A Popov after 1985, and since 1996 it has been headed by Yu S Troshkin.

In 1983, there came to a completion the first scientific-research work (the FOB-1-2 Project) concerned with feasibility analysis and engineering-economical assessment of the production of staring arrays with 16×16 and 64×64 elements, which formulated the main requirements on the material, electronics, and the requisite technological equipment, was completed. Like the situation abroad, at the first stage (1983 – 1988) the development proceeded simultaneously along two avenues — hybrid photodiode arrays (HPAs) with silicon readout and preamplification microelectronics located immediately in the area of the cooled unit of sensitive elements, and monolithic arrays on the basis of charge-transfer devices (CTDs) — CCDs (charge-coupled devices) or CIDs (charge-injection devices) of MIS structures. The development of such devices was reported in the USA already in the early 1980s [34 – 36]. Producing photodiode arrays required a high-perfection p-type material. CTDs could be developed on the basis of n-type CMT. However, n-CMT with a lifetime of 5 – 6 μs was required in this case to reduce dark diffusion currents which overfill the storage MIS cell. Neither the diode nor the photoresistive material with the requisite properties had been developed by the beginning of this research. The properties of MIS structures, which are the storage elements for a signal charge, almost completely determine the parameters of CTD-based photodetectors. The techniques of fabrication of MIS structures from CMT known at that time did not meet the basic requirements imposed on the insulator – CMT interface quality owing to a significant fixed-charge density $Q_{fc} > +10^{12}$ cm^{-2} and a high density of surface states $N_{ss} > 10^{11}$ cm^{-2} eV^{-1}. Furthermore, the then-developed dielectric coatings on the basis of CMT's native oxides, Al_2O_3, SiO_2, $YScO_3$, and the like, had a dielectric constant $\varepsilon \cong 8-20$. For an ordinary film thickness $d_i \sim 0.15-0.25$ μm, this ensured a very small storage cell capacitance $C_i \cong (1-2) \times 10^{-12}$ F assuming dimensions of 50×50 μm required for IR imaging detectors. Under high background illumination levels of 10^{17} photon cm^{-2} s^{-1} typical of IR imaging applications, such storage elements rapidly become overflown with background-produced dark carriers. Found to be no less significant were the limitations related to another dark-current component — tunnel currents arising due to a strong energy-band bending in the near-surface region of MIS structures made on the basis of narrow-gap CMT [37]. Nevertheless, in 1988, n-$Cd_{0.21}Hg_{0.79}Te$-based CID arrays with 8×8 elements (Fig. 11) were fabricated and investigated, with Al_2O_3-based MIS structures being used as the storage cells (the Baĭkal and Sova Projects). The photosignal was extracted from nonequilibrium capacity – voltage characteristics by the double-correlation-sampling technique (N G Mansvetov). Values $D^*_{\lambda\,\max} \cong (3-5)10^9$ cm Hz$^{1/2}$ W^{-1} were obtained. The above features of CMT-based CTDs called for the production of MIS structures with the use of insulators with a dielectric constant $\varepsilon \cong 10^3 - 10^4$ unknown at that time.

As a result, the main effort of matrix-detector designers was focused on the production of hybrid arrays, while the MIS technology research was aimed at the development of field-effect CMT transistors, high-quality passivating coatings, and diodes with a tunnel-transparent insulating layer (MTIS photodiodes).

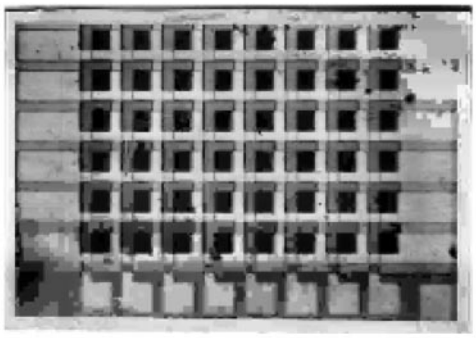

Figure 11. Fragment of a CID matrix made of n-$Cd_{0.21}Hg_{0.79}Te$ with 8×8 elements (NIIPF, 1988).

As in the years of the first CMT device developments, the material problem was among the central ones. Though the technology development for the first small-format photodiode arrays with 32×32 elements proceeded on the basis of bulk p-type single crystals, it was evident that the production of matrix detectors employing epitaxial layers held the greatest promise. Possessing, immediately after growth, a thickness optimal for radiation absorption, they do not require long and fine processing. Furthermore, the mechanical processing may produce on the p-type CMT surface a layer of the opposite type of conduction, which shunts p – n junctions. This effect, characteristic of narrow-gap CMT solid solutions, is attributed to the occurrence of 'mechanodonors' [38] — electrically active intrinsic defects in the crystal lattice stimulated by mechanical actions.

At GIREDMET, the method of liquid-phase epitaxy [39] was adopted for growing epitaxial CMT layers. At present this is the main method of industrial production of epitaxial layers by the world's leading manufacturers of multielement and photodiode arrays. The main advantages of this method are a relatively low cost and high productivity of equipment, automatic additional surface cleaning in the initial growth stage, additional purification during growth, and surface uniformity in composition. An analysis of the phase equilibrium in the Cd – Hg – Te system revealed that the growth of epitaxial layers from the tellurium-based molten solution shows the greatest promise from a technological viewpoint. In this case, the epitaxy temperature is significantly lowered, as is, accordingly, the partial mercury pressure (to 0.15 atm at $T = 500-550$ °C), while the mercury vapor pressure amounts to 1 atm even at $T = 350-400$ °C when mercury is employed as the solvent. Upon studying different versions, a technology involving layer growth in a closed volume and the final stage of removing the liquid phase from the resultant layer surface by the centrifuge method ('decanting') was adopted. Figure 12 shows the typical variation of composition with epitaxial layer depth.

The critical problem of epitaxy is choosing a right substrate for an epitaxial layer, since its properties largely define the parameters and structural perfection of the layers grown. For substrates, advantage can be taken of monatomic semiconductor (Si) or binary compounds (GaAs), as well as other materials, but in this case the presence of a 'buffer' interlayer between the substrate and the layer is required to attain a better matching of the crystal-lattice parameters. The best results were obtained when the solid solution of cadmium – zinc telluride (CZT) $Cd_yZn_{1-y}Te$

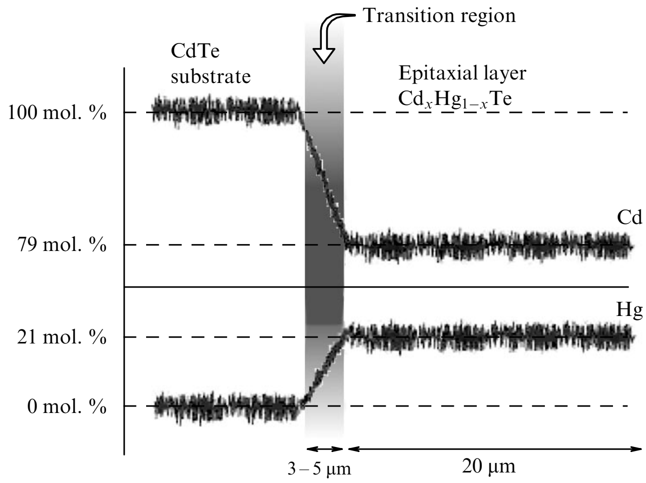

Figure 12. Composition distribution across the cleavage surface of an epitaxial layer.

($y = 0.02-0.05$) was used as the substrate. Its growth technology is rather complicated owing to the low thermal conductivity, the high vapor pressures of the components, the liability to twinning, and other factors. The method of CdZnTe single-crystal growth developed at GIREDMET (V M Lakeenkov) relies on the updated CMT crystal fabrication technology involving vertical or horizontal crystallization of the melt at temperatures of 1120–1130 °C with subsequent cooling at a rate of no higher than 10 K h^{-1}. This technology enabled obtaining single-crystal substrates, which were transparent in the IR region, with diameters of more than 30 mm and a dislocation density below $(5-8)\times 10^4$ cm^{-2} in the absence of low-angle boundaries and second-phase inclusions [40]. These works laid the foundations of the industrial production of epitaxial material for photodiodes in Russia. At the present time, the production of epitaxial layers is underway at GIREDMET.

The physicotechnological foundations of two-dimensional (matrix) photodetectors on the basis of multielement CMT photodiodes were laid at NIIPF in the course of executing the FOB-1-2, Chetkost'-MFP, Sova, Baĭkal, and Rubezh Projects (1983–1989). Three major problems had to be solved: to develop the technology of high-quality multielement small-dimension (35–50 μm) photodiodes of $Cd_xHg_{1-x}Te$ ($x = 0.2-0.3$), to develop low-noise silicon microelectronics for photosignal readout in the 'cool' region ($T = 77$ K), and, lastly, to devise a technology for combining photodiode and silicon matrices in a common hybrid microassembly. The transition to small-dimension photodiodes was necessary to provide high-resolution IR imaging instrumentation. The proximity of sensitive elements in the array called for the solution of the problem of minimizing the parasitic (electrical, optical, and photoelectric) coupling between them. In the IR range, the background illumination level is high and the temperature contrast between the objects under observation is low, and the coupling could therefore result in blurring and distortion of IR images.

An approximately 100-keV B^+ ion implantation method was developed as the principal method for producing p–n junctions for CMT photodiodes. In this case it was possible to reveal several physical features of the interaction of the ion beam with the CMT surface. The occurrence of n-type inverse layers in the near-surface region of p-type CMT was found to arise primarily from radiation defects similar to 'mechanodonors,' which emerge upon mechanical action on the CMT surface [38, 41].

The key role in multielement planar photodiode technology is played by dielectric coatings. They ensure the necessary long-term stability of parameters by passivating and protecting the surface. The passivation techniques developed for n-CMT based photoresistors proved to be inapplicable for photodiodes. In the passivation by CMT's native oxides, for instance, the high density of positive fixed charge ($\sim 10^{12}$ cm^{-2}) at the oxide–CMT interface was responsible for a high electron concentration in the near-surface region and a significant coupling between the elements even for a hole density of $\sim 10^{16}$ cm^{-3} in the substrate. Several passivation techniques were developed, including those that employ Al_2O_3, SiO_2, and plasma fluorination. Passivation with magnetron-sputtered oxygen-bearing insulators necessitated an extremely high-precision maintenance of partial oxygen pressure during film deposition, because it was found that the density of positive fixed charge at the interface was primarily related to oxygen vacancies in the insulator grown. Better reproducible results were obtained when CdTe deposited by vacuum deposition (M V Sednev) or by the 'hot wall' technique (L A Bovina, S V Golovin) was used as the insulator layer [42].

The development of Si multiplexers cooled to liquid-nitrogen temperatures commenced at NIIPF starting in the mid-1980s. The MOS transistor gate circuit was assumed as the basis, because, due to a higher storage capacitance, it is preferable to CCD registers when used in IR imaging detectors operating at significant background loads. Silicon integrated readout circuits were developed on the basis of n-MOS technology with polysilicon gates and an SiO_2 gate insulator, a small scatter of parameters, and low leakage currents of the transistor gates (A A Timofeev, E A Klimanov, V M Akimov) [43, 44]. For the photosignal readout, use was made of a circuit of direct injection of photocurrent I_{ph} (Fig. 13). The circuit comprised an accumulation capacitor C_a, an input transistor VT7, a charge storage capacitor C_s, and transistor gates VT8, VT5, VT3, and VT4, which serve to set the accumulation time for C_a and the precharging time for C_s. U_b is the bias voltage. The output of each channel is connected to the readout bus via a source follower (VT2) and a transistor gate VT1. These MOS transistor gates are combined in a two-dimensional matrix in drain and gate buses. Furthermore, the integrated microcircuit contains shift registers, accumulation sections, and control units, which form a succession of pulses applied to the gate buses of the

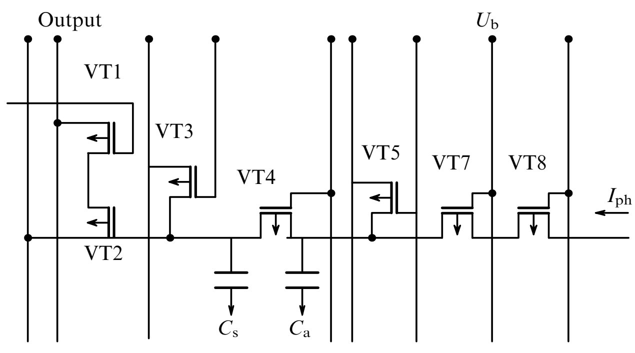

Figure 13. Circuit for direct injection of photocurrent in the photosignal readout in CMT photodetector arrays.

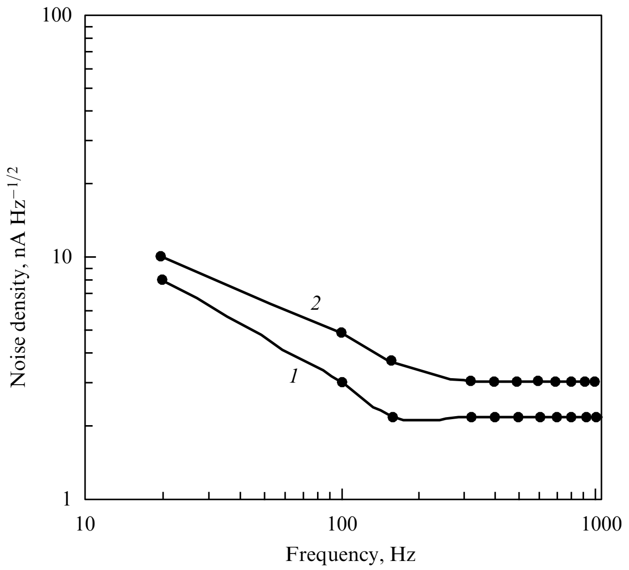

Figure 14. Noise spectra of a CMT photodiode array without (curve *1*) and with (curve *2*) a multiplexer.

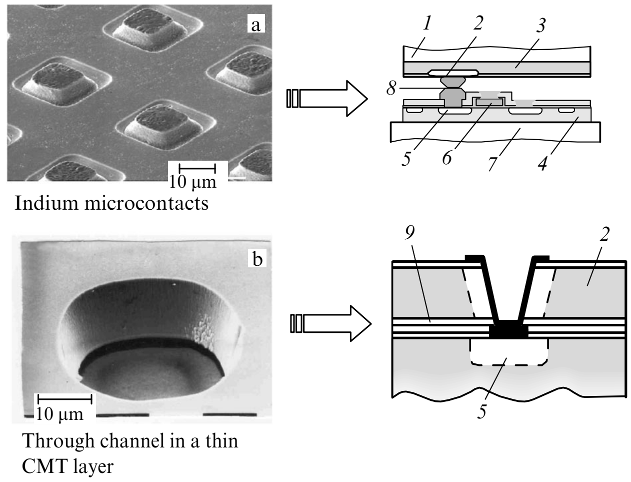

Figure 15. Different architecture of hybrid photodetector arrays built on the basis of CMT photodiodes: (a) on the basis of bump indium microcontacts; (b) employing 'vertical' p–n junctions; *1*, substrate of the epitaxial layer; *2*, n^+ region of the photodiode; *3*, epitaxial layer; *4*, silicon; *5*, source of the input transistor; *6*, gate of the second transistor; *7*, substrate; *8*, indium microcontacts; and *9*, thin p-CMT single-crystal layer.

matrix of transistor gates. The MOS gates in a closed state have leakage currents of less than 10^{-10} A and switching times of less than 10^{-9} s. Neither the current sensitivity nor the noise characteristics of the CMT photodiodes are significantly changed when the multiplexers developed are combined with the photodiodes (Fig. 14).

One of the most complicated and 'delicate' operations in the fabrication of hybrid photodetector arrays is the operation of combining the matrix of photosensitive elements with the matrix of photosignal-readout transistor gates. There, tens and hundreds of thousands of microcontacts should ensure a reliable connection between CMT photodiodes and the input devices of Si microcircuits. An analysis of possible technologies, carried out in 1983–1986, revealed that two of them hold the greatest promise: the technology of integration via bump metallic microcontacts grown on the surface of CMT photodiodes and Si microcircuits (Fig. 15a), and the technology of integration with the use of 'vertical' p–n junctions in CMT (Fig. 15b) proposed by the Mullard firm [45].

In the former case, there was a need to develop methods of growing these microcontacts on CMT and Si, as well as methods of joining them. Required in the latter case was a technology for fabricating small-dimensioned through channels in CMT by way of deep etching and the development of procedures for producing p–n junctions near the side walls of the channels. Explorations into these procedures were crowned with success in 1988: at first, there emerged a technology for the electrochemical growth of indium contacts from salt solutions (M A Batalina); later, a technology was developed for the vacuum deposition of indium and the fabrication of contacts by photolithography; and in 1989, technologies for high-frequency deep CMT etching in a mercury plasma (A V Frolov) appeared. In the last case, p–n junctions were produced by depositing thin n-type CMT layers using the 'hot-wall' technique (L A Bovina, S V Golovin). The integration that relies on 'vertical' p–n junctions is preferable for arrays made on the basis of single-crystal material. However, the progress of epitaxial layer technology brought to the fore the technology involving indium microcontacts, which still prevails in the production of CMT photodiode arrays. The equipment and technology for the procedure of integration of photodiode arrays and silicon multiplexers using the 'cold'-welding method were developed by the late 1980s (V N Golovin, V Yu Ivanov).

The first CMT-photodiode-based arrays with 32×32 elements, intended for the 1.5–2.5, 3–5, and 8–12 μm spectral ranges, were fabricated and investigated in 1988–1992. They were grown by isothermal-epitaxy methods on CdTe substrates and by liquid-phase epitaxy on CdZnTe substrates [46, 47]. The main photoelectric parameters of these arrays are collected in Table 2. The variance of current sensitivity calculated for efficient elements (> 98%) does not exceed 30%. The first results on staring arrays of format 128×128 were obtained during the same period.

In the fabrication of arrays of format 128×128 and larger, the requirements on the uniformity of electrophysical parameters and surface quality of the initial material are significantly more stringent. Departures from planeness or surface asperity greater than 2–3 μm make samples unsuited for the operation of joining with silicon multiplexers. The second half of the 1990s saw the development of production technology of detector arrays with the number of elements ranging from 128×128 to 384×288 [48] (Fig. 16). The average values of specific detectivity at $T = 80$ K are equal to 4.2×10^{10} cm Hz$^{1/2}$ W^{-1}, the fraction of faulty channels being less than 3%. The measured value of noise-equivalent

Table 2. Main characteristics of photodetector arrays of size 32×32 (NIIPF, 1988–1992).

Cutoff wavelength	Pitch, μm	Current sensitivity, A W^{-1}	Detectivity, cm Hz$^{1/2}$ W^{-1}	T_{oper}, K
2.8	70	1.1	2.4×10^{10}	300
4.0	70	1.5	2.5×10^{10}	190
9.4	150	3.0	4.1×10^{10}	80
1.5	70	4.0	1.7×10^{10}	80
13.0	150	5.2	1.1×10^{10}	80

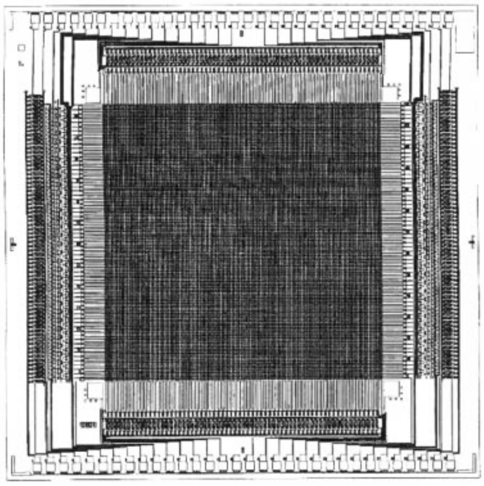

Figure 16. Staring photodiode array of format 128 × 128 (NIIPF, 1996).

temperature difference, i.e., the resolvable temperature contrast, is $\Delta T < 0.1$ K.

Almost simultaneously with the staring arrays, at NIIPF a start was made on the development of multirow arrays of dimensions M × N (M is the number of rows and N is the number of elements in a row) for the time-delay-and-integration (TDI) operating mode in systems with optomechanical scanning. Several versions were pursued for the array of size M × N: 4 × N and 2 × 2N. Figure 17 shows the difference between them. Unlike detectors with internal photosignal integration, in this case a summation of the signals from elements arranged in rows occurs. As a result, the detection ability of the device rises by a factor of about $\sqrt{M}$. In detectors of sizes 4 × N and 2 × 2N, the detection ability is therefore 2 – 1.4 times higher as compared to devices of size 1 × N. Devices of size 4 × N possess a higher detectivity but necessitate interlaced scanning.

To combine rectangular-shaped photodiode TDI arrays (about 4 × 12 mm) with silicon multiplexers, a special technology involving joining via an intermediate sapphire raster was developed, with indium microcontacts being grown on the metallic stripes of the raster (Fig. 18). By the end of the 1990s, CMT photodetector arrays of formats 4 × 16, 2 × 32, 4 × 48, 2 × 96, 4 × 128, and 2 × 256 were developed at NIIPF.

A serious challenge in the production of photodetector arrays for IR imaging was the development of methods and equipment for controlling their parameters, which were significantly different from those developed for few-element

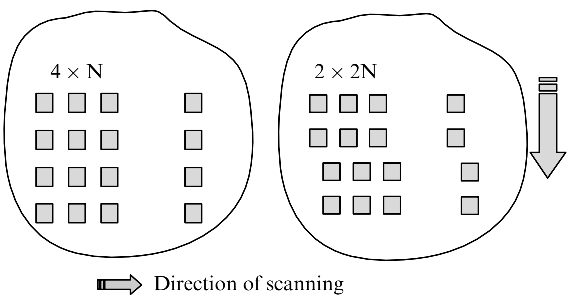

Figure 17. Topology of TDI arrays of sizes 4 × N and 2 × 2N.

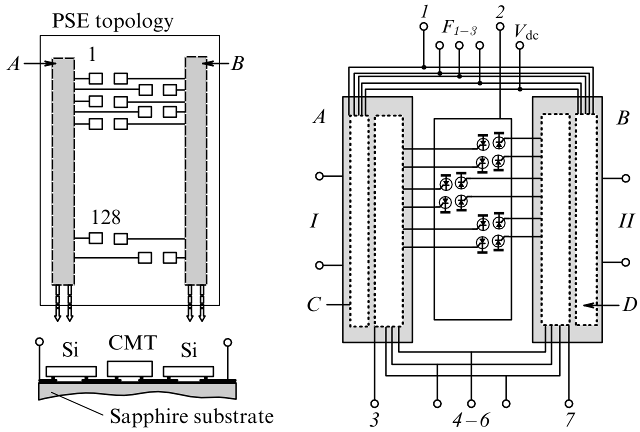

Figure 18. Unit of photosensitive elements (PSEs) of a TDI arrays of size 2 × 256 made of CMT: *A*, multiplexer of the elements 1....128 and 257....384; *B*, multiplexer of the elements 129....256 and 385....512; *C*, *D*, shift registers; *I*, *II*, multiplexed photosignal outputs; *1*, *2*, common leads of the array of photodiodes and of the shift registers, respectively; F_{1-3}, V_{dc}, pulsed voltage and dc voltage for controlling the shift registers; *3*, *7*, photodiode bias control buses; and *4* – 6, photosignal readout control buses.

devices. Indeed, access to photodiodes (which exceed 100 thousand in a photodetector array of size 384 × 288) is possible only via a silicon multiplexer, whose dynamic shift register can connect one element to the measuring system for a fraction of a second to subsequently connect the input of the measuring system to other elements. Subtracting the multiplexed signal from dark currents makes inevitable the use of microprocessor digital processing. TDI arrays have output buses to which the signals from each row containing between 16 and 128 sensitive elements are brought out in parallel. This organization of the operation of a photodetector module necessitates the use of sampling techniques for measuring the parameters of each element, which enable pinpointing and measuring a preselected section in the video signal under investigation pertaining to a specific photosensitive element. The construction principles of flexible automated measuring systems that make it possible to investigate detector arrays at frequencies of 10 – 50 frames s^{-1} were developed at NIIPF during the period of 1990 – 1999 (V N Solyakov, K O Boltar').

Table 3 shows recent results on the development of arrays at NIIPF.

The Siberian Scientific-Research Institute of Optical Systems (NIIOS, Novosibirsk) joined the work on the problem of photodetector arrays in the first half of the 1980s. NIIOS took up the development of the techniques and means for processing IR images obtained using multielement CMT detectors. A special feature of the IR range and the photodetector devices employed in this range is that the background and dark components of the signal exceed, and sometimes significantly exceed, the desired signal. Another feature is related to a substantial difference in responsivity and dark current between the elements, which produces structural noise and masks the object images on a low-contrast thermal scene. This called for the development of algorithms and special circuits as well as the production of special-purpose microprocessor devices to ensure the equalization of the responsivity of elements, referencing to the zero level, the subtraction of the background constituent, the

Table 3. Parameters of CMT arrays (NIIPF, 2002).

Number of elements	Topology	Element size, μm	Pitch, μm	Cutoff wavelength, μm	Aperture angle	Detectivity, cm $Hz^{1/2}$ W^{-1}
32×32	$N \times N$	40×40	70	10.5	60°	$(3-4) \times 10^{10}$
128×128	$N \times N$	30×30	35	10.5	60°	$(3-4) \times 10^{10}$
384×288	$N \times N$	30×30	35	10.5	60°	$(2-3) \times 10^{10}$
4×48	$4 \times N$	30×30	60	10 – 10.5	60°	$\geqslant 7 \times 10^{10}$
2×96	$2 \times 2N$	30×30	60	10 – 10.5	51°	$\geqslant 5 \times 10^{10}$
2×256	$2 \times 2N$	35×35	70	10.5 11.5 12.5	64°	$(4-5) \times 10^{10}$

'replacement' of defect channels, and other techniques (I S Gibin, A N Potapov, N M Maleev, et al.) [50].

At present, CMT-photodiode-based arrays represent complicated photoelectronic information complexes. Apart from the photodiode array and cooled photosignal readout microelectronics, these complexes comprise a microcryogenic cooling system and special microprocessor digital devices, which provide at output a sequence of IR-image signals in the standard television format.

4. Hybrid linear detector arrays. MIS- and MTIS-structure-based devices

One more avenue of research on detectors with photosignal preprocessing microelectronics located in the region of sensitive CMT elements was developed at NIIPF in the second half of the 1980s. The main objective was the development of technological production processes for photodetectors with the number of elements ranging up to 128 and an internal switching of photosignals in the cool region, which drastically reduced the number of leads from the vacuum cavity. This improved the reliability of the design and lowered the heat fluxes (the Rubezh and Selenga Projects; scientific supervisor: V P Ponomarenko). Figure 19 depicts a unit of photosensitive elements of one of these photodetectors. Located at the center of the sapphire raster is a linear photodiode array of size 1×128, with pairs of 32-channel MOS switches made on the basis of transistor gates and the corresponding shift registers arranged on either side of the array. The leads from the cool detector region do not exceed 30 in number.

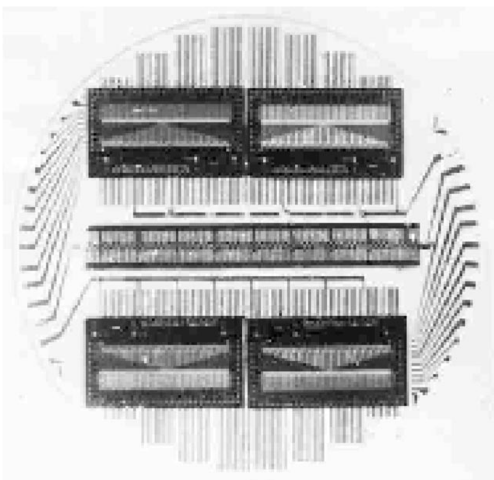

Figure 19. Photosensitive element unit of a hybrid photodetector made on the basis of CMT photodiodes Rubezh with 1×128 elements (NIIPF, 1989).

For the sensitive elements of such hybrid detectors, use was made of photodiodes with a p – n junction, as well as of a new type of diode structure — Schottky photodiodes with a tunnel-transparent insulating layer (MTIS) developed in the course of the execution of the Rubezh Project. Classical Schottky barriers produced by deposition of different metals on a CMT surface had not gained widespread acceptance because of the high density of surface states at the CMT – metal interface. The presence of an ultrathin passivating layer between the metal and CMT could eliminate this drawback and lead to the advent of a new type of high-sensitivity element for recording IR radiation. For an insulator thickness of 5 – 9 nm, the barrier produced by this ultrathin dielectric layer is so narrow that the carriers easily tunnel through it. Oxides and fluorides obtained by plasma anodizing of the surface and the 'foreign' insulators Al_2O_3 and SiO_2 proved to be candidates for tunnel-transparent passivating layers. Photosensitive structures with 2×128 elements were produced on the basis of such MTIS photodiodes to exhibit an average detectivity $D^*_{\lambda\,\max} = 3 \times 10^{10}$ cm $Hz^{1/2}$ W^{-1} [56]. MTIS diodes proved to be efficient sources of electron injection, allowing for their use as drain – source elements in p-CMT-based field-effect transistors. Late in the 1980s, this resulted in the advent of a new type of field-effect transistors with an MTIS structure based on narrow-gap solid solutions [57].

The first information from abroad on the production of field-effect transistors with an insulated gate on the basis of bulk single crystals and epitaxial layers of CMT dates back to 1980 [51, 52], and in 1989 the fabrication of a simple digital microcircuit relying on CMT transistors was even reported [53].

The work aimed at the production of CMT-based transistors was initiated at NIIPF in 1984 (the Selenga Project). The first n-channel MIS transistors with a channel length $L = 60$ μm [54] were obtained by 1986 (Fig. 20). The problem of the development of the MIS gate structure proved to be one of the central ones in their production. The quality of interfaces in these structures should be extremely high to ensure the effective source-to-drain transfer of injected carriers. An investigation was made of several methods for producing gate insulators: plasma anodizing and fluorination, various ways of depositing Al_2O_3 and SiO_2, and other

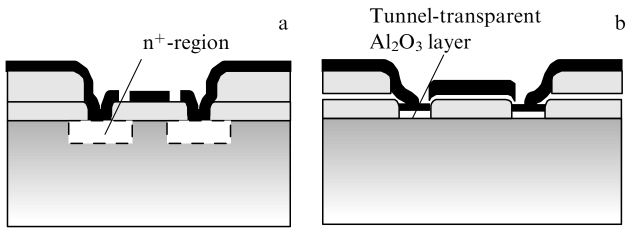

Figure 20. Field-effect transistors of CMT developed at NIIPF (1988): (a) n-channel field-effect MIS transistor made of p-$Cd_{0.2}Hg_{0.8}Te$; (b) n-channel field-effect transistor with an MTIS structure made of p-$Cd_{0.2}Hg_{0.8}Te$.

methods. Finally, the Al_2O_3 film deposition by high-frequency magnetron sputtering in an oxygen-bearing plasma proved to be most favorable from the technological standpoint. The following Al_2O_3 – CMT interface parameters were realized in this case: a positive fixed charge density $Q_{fc} = (3-6) \times 10^{10}$ cm^{-2}, a density of fast surface states $N_{fs} < 10^{11}$ cm^{-2} eV^{-1}, and a density of slow surface states $N_{ss} \sim 10^{10}$ cm^{-2} eV^{-1}. This made it possible to produce the Soviet Union's first field-effect long-channel p-$Cd_{0.2}Hg_{0.8}$Te-based transistors with a steepness of the output characteristics in the linear section $g^* = 1.4-1.5$ mA V^{-2} (I V Shimanskiĭ, E A Salmin, V P Ponomarenko).

Such structures proved to be extremely useful in the investigations of minority charge carrier transfer in the surface layers of narrow-gap solid solutions. New quantum size effects were discovered and investigated near the insulator – p-CMT interface. Here, owing to the small effective mass, the electron wavelength $\lambda_n = h/2\pi(m_n^* kT)^{1/2}$ proves to be comparable with the thickness of the space-charge region in the near-surface region of the MIS structure $l_n = kT/qE_s$ (E_s is the transverse field near the surface of the MIS structure). As a consequence, the field dependences of electron mobility in inversion channels (for instance, in the gate region of the transistor region) exhibit several features arising from the two-dimensional nature of the electron gas and the quantization of motion in the direction perpendicular to the surface. These investigations enabled the determination of the main properties of charge-carrier-transfer effects in the near-surface layers of narrow-gap solid solutions [55].

5. Conclusions

The previous decade may be characterized as a period of swift and fruitful development of the technologies of cadmium – mercury telluride and devices made on its basis. The foundation laid in the 1960s – 1980s by the researchers at NIIPF, GIREDMET, the Siberian NIIOS, the Factory of Pure Metals, and many other institutions has made it possible to solve, despite the complicated period of reorganization of domestic science and industry, the major scientific and technical problem of the development of the element base for new-generation instruments of IR imaging, IR direction finding, laser ranging and communication, high-perfection CMT single crystals and epitaxial layers, as well as infrared matrix photodetector devices based on them. Despite the abundance of new ideas and methods for recording IR radiation in the 8 – 14 and 3 – 5 μm ranges (quantum wells, superlattices based on wide-bandgap semiconductors, and other structures), these devices, along with microbolometers and InSb-, PbSe-, PbS-, and PtSi-based photodetectors, will most likely prevail in optoelectronic instrument building in the near future.

The possibilities of the technologies reviewed in this paper have by no means been exhausted. Their employment in the nearest future will result in the production of larger-sized photodetector arrays for IR imaging. Nor have the possibilities of photoresistor technologies been exhausted: the use of ideas and techniques for combining photosensitive elements with cooled silicon photosignal-processing microelectronics, which were initially devised for photodiodes, may bring into being multielement hybrid photoresistors with 10^3 or more elements.

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