PHYSICS OF OUR DAYS

Wide-band II-VI semiconductors and the prospects of their application

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1. INTRODUCTION

The rapid development of electronics, involving the application of crystalline semiconductors and insulators, has contributed to an appreciable expansion and deepening of our knowledge of the structure of solids and has yielded most valuable information on the physical processes that occur in them.

In turn, progress in the development of electronic semiconductor devices is caused to a considerable degree by the accomplishments in the technology of producing pure and specially doped materials, which has made it possible to vary the crystal properties in the desired direction. The first to be "mastered" in this respect were the elemental semiconductors germanium and silicon. Specially purified specimens of these materials contain less than one impurity atom per 10^{12} atoms of the host material. Germanium and silicon were the materials from which the principal elements of semiconductor electronics, diodes and transistors, were developed. Subsequently, III-V semiconductors (compounds of elements of the third and fifth group of the periodic system) have found wide use, especially in semiconductor lasers, tunnel diodes, and Gunn diodes.

Progress in science and technology continuously adds to requirements imposed on semiconductors, and calls for the development of new materials; nonetheless, the number of "mastered" semiconductor materials is still small.

Recently, in connection with new problems of semiconductor technology, semiconductor specialists have become greatly interested in the traditional luminescent materials—II-VI compounds with wide forbidden bands, principally in connection with the problem of the development of elements for optoelectronics and acoustoelectronics. These compounds have long been used for the better powdered luminors (for many applications), but to solve most problems in semiconductor technology it is necessary to have large crystals and single-crystal films with specified electrical and optical properties, as well as p-n junctions. The preparation of such samples is greatly hindered by the tendency of these compounds to form various intrinsic defects, to deviate unilaterally from stoichiometry, and also to have a high melting temperature in comparison with the sublimation temperature. Nonetheless, the development of modern technological methods has already led to certain progress in the preparation of semiconducting materials based on these compounds, and promises even more in the future. Among these methods are gas-transport crystal-growth methods, crystal growth from the melt at high inert-gas pressure, preparation of films by ion evaporation and vacuum, and ion doping.

Obviously, the possibilities of using the entire class of compounds are quite extensive and cannot be described in a relatively brief review. Attention is therefore focused in this article on problems that cannot be solved or are very difficult to solve by using other compounds.

We consider the compounds ZnS, ZnO, ZnSe, ZnTe, CdS, CdSe, CdTe and their solid solutions.

2. TECHNICALLY PROMISING SPECIFIC PROPERTIES OF WIDE-BAND II-VI SEMICONDUCTORS

A characteristic feature of II-VI compounds is the possibility of formation of various types of point defects, impurity and intrinsic, in crystals grown on their basis, with a great variety of different defect complexes as well as stacking faults. In many cases these defects play a beneficial role: thus, point defects can act as luminescence and photoconductivity centers and can serve as donors and acceptors, while stacking faults produce in ZnS an anomalously large photovoltaic effect reaching hundreds of volts.

In many cases, however, the presence of various defects is highly undesirable. This will be discussed in greater detail when particular examples are considered. We emphasize here only that the problems involved in the technology of II-VI compounds are connected mainly with controlling the defect structure of the obtained materials.

The widths of the forbidden bands of the compounds considered by us and of their solid solutions correspond to the total spectrum of the visible light and in part to the ultraviolet region (Table I). This makes it possible to use them in principle as semiconducting sources and receivers for visible and ultraviolet light. No less important is the fact that in crystal phosphors prepared

TABLE I. Forbidden-band widths E_g and effective masses and mobilities of electrons (n) and holes (p) in II-VI compounds

Compound	E_g, eV ($T \approx 300$ °K)	Effective masses[b]		Mobilities, cm²/V-sec ($T \approx 300$ K)	
		m_n	m_p	μ_n	μ_p
ZnS hexagonal	3.74[1]	0.28 ⊥ c *)[4] 0.39 5c	0.49 ⊥ c[4] 1.4 ‖ c[4]	140[16]	5[16]
ZnS cubic	3.66[1]	0.39 5c			
ZnO	3.25[2 a]	0.28[6]	1.8 ⊥ c[12] 0.6[13]	110[17]	
ZnSe	2.73[2 a]	0.17[7]			
ZnTe	2.23[3]	0.09[8]	0.6[14]	530[18]	28[23]
CdS	2.53[1]	0.205[9]	0.7 ⊥ c[9] 5.0 ‖ c[9]	340[19] 350[20]	110[16] 15[24]
CdSe	1.85[1]	0.13[10]	0.45 ⊥ c[15] ⩾ 1 ‖ c[15]	720[21]	75[21]
CdTe	1.50[2]	0.096[11]	0.41[16]	1000[22]	70[25]

[a]Values calculated from the data of [²]. [b]Values in electron-mass. [c]Theoretical value.

*The symbols ‖ and ⊥ indicate that the values of the effective mass are connected with a direction parallel or perpendicular to the c axis of a crystal with hexagonal structure.

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from these compounds the electronic radiative transitions have high probability; they have consequently been long used as effective photoluminors, cathode luminors, and electroluminors (for example, the photoluminescence quantum yield of good luminors based on ZnS is close to 100%). This is due to the large depth of the levels of the luminescence centers and to the associated low probability of conversion of the excitation energy into thermal vibrations of the crystal lattice, since such a conversion corresponds to simultaneous production of dozens of phonons.

It is very likely that no other class of semiconducting materials exhibits so broad a luminescence-center spectrum, extending from the ultraviolet to the infrared, as do the II-VI compounds.

The same can be said of the photosensitivity centers. This circumstance, in conjunction with the large mobility of the electrons and holes in the II-VI semiconductors (see Table I[1]) in comparison with their mobility in other compounds with an equally wide forbidden band, makes it possible to use them for the construction of better photoresistors for short-wave light.

However, even greater possibilities for the development of sources and receivers of visible and ultraviolet light is afforded by an important intrinsic property of wide-band II-VI semiconductors, namely, the presence of "direct" bands in them, i.e., the coincidence, in quasimomentum space, of the maximum of the valence band with the minimum of the conduction band. This contributes to a high efficiency of intraband radiative recombination of the electrons and holes, and also to generation of electron-hole pairs in the absorption of short-wave light. The presence of such "direct" bands is a fundamental requirement for semiconductor lasers.

Owing to the ability of II-VI compounds to form solid solutions, it is possible to vary the width of the forbidden band in a wide range, and to vary by the same token the recombination-radiation spectrum and the photosensitivity.

The crystal structure of II-VI compounds, whether hexagonal or cubic without symmetry center, gives rise of a strong piezoeffect in these compounds (for example, CdS is approximately ten times more effective than quartz in this respect). This is used in various acousto-electric devices such as ultrasound amplifiers, active delay lines, detectors, strain gauges, etc. In addition, these crystals are subject to an optical nonlinearity that can be used to obtain laser harmonics (to increase the laser frequency) as well as difference frequencies by mixing modes of different lasers (to decrease the laser frequency), so as to obtain submillimeter waves.

3. PRINCIPAL TRENDS IN THE USE OF WIDE-BAND II-VI SEMICONDUCTORS

a) **Optoelectronics elements.** A new branch of science and technology, optoelectronics, has been rapidly developing in recent years. Unlike ordinary electronics, they function not with electric but with optical signals. This extends the frequency range in many cases, makes it possible to employ the advantages of coherent radiation and to decrease the dimensions of the devices, improves their interference immunity, etc.

Optoelectronics is a very broad concept, including many various devices, foremost among which are

luminescence and laser sources as well as light receivers that are spectrally conjugated with them. Some of these sources and receivers possess memory, owing to peculiarities in the kinetics of the processes that occur in them, or else through artificial complication of their structure by adding various types (electrical, magnetic, or optical) of memory elements. By combining these devices it is possible to develop complicated structures for computer technology, for information display, or for automation devices (optrons), light and image converters and amplifiers, converters for various types of radiation, etc.

Optoelectronics as a branch of science entails observation and investigation of phenomena that can serve as the basis for optoelectronic technology elements, and also the study of functional communication by means of optical signals, namely signal formation, signal propagation in active and passive media, signal input and output, etc.

We begin this section with a consideration of problems involved in the development of the various light sources based on II-VI compounds.

1) Lasers with electronic excitation. The first to observe lasing by excitation with an electron beam were Basov, Bogdankevich, and Devyatkin, using CdS[26]. Lasing was subsequently obtained also in CdTe[26], CdSe[28], ZnS[29], ZnSe[39], and in crystalline CdS_xSe_{1-x} solid solutions[31].

These lasers can be used to solve many problems mainly because of the unique features of their excitation.

Foremost among these features is the use of homogeneous undoped crystals. The technology of the manufacture of such samples is simple enough in comparison, say, with the technology of injection lasers or even electroluminescent light-emitting diodes (see the next section). No less important is the fact that in these lasers it is easy to control the light beam, since one can use for this purpose the well-developed systems for the control of electron beams (focusing, modulation, scanning). Further, by electron excitation of II-VI compounds it is possible to obtain light pulses on the order of one megawatt at a high repetition frequency, and at a beam divergence of only several minutes[32]. In addition, the use of II-VI compounds and of the solid solutions makes it possible, as already noted, to cover the entire visible and near-ultraviolet spectrum.

These lasers are needed for spectroscopy and biological research, and to solve a number of technical problems.

In particular, high-power green lasers are needed for underwater research. Sea water, as is well known, has a so-called "transparency window" in the green region of the spectrum. The best material for this purpose, from the point of view of the optical characteristics, seems to be CdS.

Ultraviolet lasers, including those of high-power, are needed to record information in computers. This technique is based on the coloring of a film made of a mixture of spiropyrine and tribromophenol by ultraviolet irradiation. The film sensitivity is $\approx 5 \times 10^{-2}$ J/cm². A system for recording of this type is being developed by the Telefunken Company (West Germany). A writing density of $\approx 10^7$ bit/cm² has already been attained
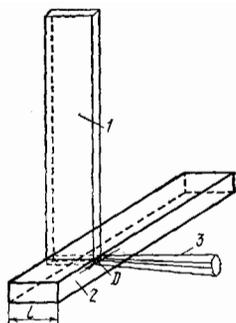
FIG. 1. Diagram of semiconductor laser with transverse pumping by an electron beam. 1—Electron beam, 2—semiconductor crystal, 3—laser beam.
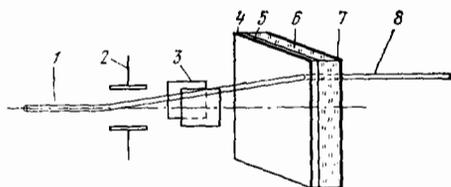

FIG. 2. Diagram of semiconductor laser with longitudinal pumping by an electron beam. 1—Electron beam; 2, 3—deflecting-system electrodes; 4—100% mirror; 5—semiconducting single-crystal layer; 6—substrate; 7—semitransparent mirror; 8—laser beam.

(private communication). This is 10^3 times larger than obtained with magnetic recording. The ultraviolet light is generated by doubling the frequency of an argon laser with the aid of a nonlinear element. The problem can be simplified by using a solid-state ultraviolet laser. The best material for this purpose seems to be ZnS.

The relative simplicity with which an electron beam can be controlled is presently used to develop systems with scanning of the laser beam in space (scanning lasers). These systems are based on two types of lasers, which differ in the type of the sample and in the mutual directions of the electron and laser beams.

In the first case[33] (Fig. 1) the sample is a rod of rectangular cross section, two opposite faces of which form the resonator, the excitation being effected through one of the other faces. The electron beam, whose intensity is modulated by the control signal, moves along the rod. Lasing is produced in that part of the rod on which the beam is incident at the given instant. The laser beam emerges through the semitransparent resonator mirror, and its direction is perpendicular to the direction of the electron beam. This laser is called transversely-pumped. When used by itself, it ensures only one-dimensional scanning of the light beam. It is possible, however, to obtain two-dimensional scanning by adding to the system a rotating prism or mirror.

In the second case[34] (Fig. 2), the sample is a plane-parallel plate whose surfaces serve as the resonator mirrors. The electron beam, controlled by a two-coordinate deflecting system, moves over the surface of the sample, penetrates through the mirror coating, and excites lasing in the corresponding part of the semiconducting plate. The light emerges through a second partially-transparent mirror of the resonator. Two-dimensional scanning by the light beam is obtained in this case directly. Since the laser beam is oriented along the electron beam, this type of laser is called a laser with longitudinal pumping. The length of the active zone in such a laser is determined by the depth of penetration of the electrons, so that a relatively high voltage, $\gtrsim 50$ kV, is needed for their acceleration. For a laser with transverse pumping, 15—20 kV suffice.

The frequency of scanning lasers can be rapidly tuned if the rods are made of solid solutions of II-VI compounds with a composition that varies along the rod[31].

Scanning lasers will probably find use in projection television[35], including color television, and in systems for information display on large screens (several square meters). The point is that the brightness of cathode-ray tubes with laser screens are larger by two or three orders of magnitude than the brightness of modern television projection tubes with luminors.

For projection color TV it is necessary to use a three-component kinescope with lasers that emit red, green, and blue light. The material can be CdSe for the red laser and CdS for the green laser. The main problem in the development of such a kinescope is that of the blue laser; in our opinion, the best materials for this purpose can be obtained on the basis of ZnSe, ZnS_x, Se_{1-x}, and $Zn_xCd_{1-x}S$.

No less important a trend in the use of scanning lasers is their employment as address switches in large-capacity optical memories. The operating principle of such a switch[36] consists of aiming the electron beam on that part of the screen from which the laser beam goes to a hologram selected from a matrix of many holograms, and makes it possible to "read" it with the aid of a photoreceiver matrix or an image converter.

Modern light-sensitive materials make it possible to record holograms containing 10^6-10^7 bit/cm^2. The development of an address tube for 10^5-10^6 discrete positions of the optical beam makes it possible to store $\sim 10^9$ bit on a photographic plate measuring ~ 100 cm^2. The screen emission should correspond to the maximum sensitivity of the photoreceivers. For photomultipliers, this maximum occurs in the green or blue region. The most promising materials in this case are CdS, CdS_xSe_{1-x}, $Zn_xCd_{1-x}S$, ZnSe, and ZnS_xSe_{1-x}.

To solve most of the foregoing problems it is necessary to have large structurally-perfect single crystals with linear dimensions on the order of several centimeters, without block structures, with a minimum number of stacking faults and dislocations $(< 10^3$ cm$^2)^{3)}$, and also single-crystal plates or epitaxial films with areas on the order of several square centimeters and thicknesses $\gtrsim 10-50$ μ. Preliminary research results show that crystals grown from the melt are not suitable for this purpose.

2) Electroluminescent light sources. The wide spectral ranges, the high probability of radiative transitions, and the relatively good mobility of the carriers of wideband II-VI semiconductors have naturally attracted the attention of many researchers wishing to obtain an effective conversion of electric energy into visible or ultraviolet light.

From this point of view, powdered electroluminors based on ZnS have been intensively investigated since the early Fifties. The electroluminescence of the powdered ZnS-Cu luminor mixed with a dielectric and placed in a capacitor to which an alternating voltage is applied was discovered in 1936 (the Destriau effect)[37]. One of the capacitor electrodes is transparent and the light passes through it. The advantage of powdered

electroluminors is that they can be readily used for the construction of flat non-vacuum light sources of relatively large area, which are widely used in illuminated display panels, control scales, mnemonic circuits, solid-state screens etc. By matching the spectral characteristics of electroluminors and photoresistors (also based on II-VI compounds) one can develop various optoelectronic systems such as automatic-control devices (optrons), amplifiers and converters, e.g., for x-ray radiology.

The energy efficiency of the best laboratory samples of electroluminescent capacitors is ≈2%, i.e., almost the yield of incandescent lamps. The energy consumption is ≈1 mW/cm² of screen, and the brightness is ≈300 nit (voltage 220 V at 400 Hz). In our opinion, the progress in optoelectronic technology, based on the use of powdered electroluminors, is no longer determined by the progress and the technology of their preparation. The peak in the results of this technology has been reached approximately ten years ago[3] by which time the principal papers devoted to the mechanism of the Destriau effect have already been published[38-44][4].

What is needed at present is the development of a commercial technology for electroluminescent capacitors, including control over the granulometric composition of the luminors, and the use of transparent insulating binders with large dielectric constant ($\epsilon \gtrsim 10$), capable of protecting the luminor against the action of atmospheric moisture and oxygen.

Many problems of technology of electroluminors call for the development of optoelectronic devices, electric communication systems, and other elements, especially low-inertia photoresistors. Specialists of the Siemens concern (West Germany) are investigating for this purpose ZnO (private communication), which in this respect is better than the presently used CdS and CdSe.

A very important problem is the development of electroluminescent oscilloscope and television screens. Such screens are voltage-scanned. They offer many advantages over cathode-ray tubes. First, there is no need for an evacuated tube; second, the required voltage is lower by at least one order of magnitude than the accelerating voltage of a modern television kinescope; third, the thickness of the screen becomes much less than its width and height.

The first operating models of electroluminescent television screens were produced by the specialists of the Japanese concerns Matsushita[45] and Mitsubishi[46]. The first model is based on the electroluminor ZnS-Cu, Al. The scanning is over 230 vertical and as many horizontal electrodes (52 900 image elements). The brightness is voltage-modulated.

In the Mitsubishi model, the number of image elements is 80 × 80, the luminor is ZnS_xSe_{1-x}-Cu, Br with x = 0.7. This luminor produces a larger image contrast than ZnS-Cu, Al. The brightness is modulated by the number of voltage pulses.

The exciting voltage is 300—400 V in the first model, and 450 V in the second. The power supplies are relatively large.

Electroluminescence of light sources having no dielectric binder usually occurs at lower voltages. This includes electroluminescence of sublimated films, "domain" electroluminescence[5], and in particular re-

combination radiation of semiconductors, produced when minority carriers are injected in them (injection electroluminescence). This includes, in particular, the luminescence of forward-biased p-n junctions; in this case the needed supply voltage is approximately equal to the width of the forbidden band, i.e., only several volts. This is very important, for in this case one can use small integrated-circuit power supplies. From the point of view of efficiency, injection electroluminescence is likewise most promising. As is well known, in this case the theory predicts an energy yield of ~100%[47]. However, the actual efficiencies of injection sources based on II-VI compounds are still close to the efficiencies of electroluminescent capacitors.

The point is that the development of effective injection sources of light based on II-VI semiconductors encounters great difficulties, due to the tendency of the defects in these semiconductors to become mutually compensated (donors by acceptors), leading to a low electric conductivity, and due to the tendency to form a single type conductivity, so that the preparation of p-n junctions becomes difficult[8]. Thus, for example, the obtained ZnS, ZnO, ZnSe, CdS, and CdSe crystals are only of the n-type, and the ZnTe crystals are of the p-type. The reason is that these crystals are usually grown and doped at high temperatures, at which electroneutrality is ensured during the doping process not by the free carriers but by charged vacancies that are produced at these temperatures[49,50].

In addition, in all the II-VI compounds, especially in the sulfides and selenides, additional factors can act and interfere with their synthesis in the form of n- or p-type with low resistance. First, the solubility of the suitable acceptor impurities may be too low (i.e., less than the minimum donor impurity concentration attained at the present time in the purification process) and, second, the impurities may not enter in the required form. For example, a metal of the first group (acceptor impurity), may form a donor when it lands in an interstice.

Let us dwell in greater detail on the present status and prospects of the development of injection light sources based on wide-band II-VI semiconductors.

A p-n junction was produced in[51] by diffusion of Al and Cd donor impurities into p-type ZnTe. Injection electroluminescence was observed in this junction starting with 2.5 V. The emission maximum was at 575 nm. The quantum yield was approximately 1% at 77°K.
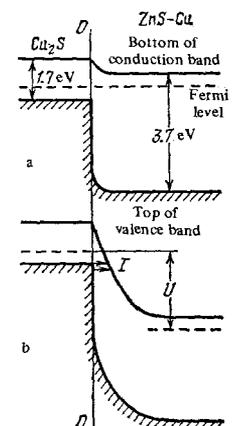
FIG. 3. Idealized band scheme of Cu_2S-ZnS heterojunction: a) at equilibrium; b) when a voltage U in the opposite direction is applied. I—electron tunneling.

In ZnS, p-n junctions were obtained by diffusion of Cu and Ag acceptor impurities in a high-resistance n-type crystal ($\sim 10^8$ Ω-cm)[52-54]. Injection electroluminescence was observed starting with approximately 2 V. The luminescence spectrum contained a blue band and an ultraviolet band with maxima at 450 and 360 nm, respectively. The external quantum yield was ~0.1% at room temperature.

Better light-emitting diodes were obtained, however, with solid solutions. First among them is $ZnSe_xTe_{1-x}$ with $0.4 \leq x \leq 0.5$ (p type). The p-n junctions were obtained by diffusion of aluminum. The diode produces red light with a maximum near 625 nm. The external quantum efficiency is $\approx 18\%$ at $70°K$[55]. Next comes $Cd_xMg_{1-x}Te$ (x = 0.65). The light-emitting diodes were prepared by diffusion of P and Cd. The maximum of the emission occurs at 680 nm[56-58]. The efficiency reaches $\approx 1\%$ at room temperature (private communication).

We indicate for comparison that a similar efficiency is possessed by the better light-emitting diodes based on III-V compounds, which are presently used in optoelectronics for the visible region of the spectrum. Thus, the "red" GaP light-emitting diodes of the West-German concern "Siemens" and of the Japanese concerns Matsushita and Toshiba have efficiencies 1—2%, while the "yellow" and "green" diodes have 0.2%). It should be noted here that the cost of diodes based on gallium compounds is higher by approximately one order of magnitude. The specialists of the Matsushita concern, who have developed a $Cd_xMg_{1-x}Te$ diode, state that its use in numerical indicators of portable computers, in place of GaP diodes, can lower the cost of these computers by a factor 2—3 (private communication).

However, light-emitting diodes based on II-VI compounds and obtained by thermal diffusion usually produce a much lower brightness than II-V light -emitting diodes. The reason is the high resistance of both the initial crystals and of the regions in which the conductivity is inverted by thermal diffusion. Nonetheless, the relatively high efficiency of injection luminescence of light-emitting diodes that are far from perfect gives grounds for hoping to realize an effective injection light source based on the wideband II-VI compounds. This returns us to the problem of overcoming their tendency to mutual compensation of the defects and of obtaining low-resistance materials of the n- or p-type.

The feasibility in principle of overcoming these tendencies and of controlling the electric properties of the wide-band II-VI compounds is uncovered by the ion-doping method[7]. Ion doping can be carried out at relatively low temperatures, at which the thermal-equilibrium vacancy concentration is low and the vacancies are unable to compete with the free carriers in the maintenance of electroneutrality. The point is that in the cases of interest to us the enthalpy of vacancy production exceeds the energy released by electron transfer from a vacancy to the introduced impurity (the compensation process), i.e., this energy is insufficient for vacancy production. To produce a vacancy it is necessary to have an appreciable increment of thermal energy, so that the compensation process does not play a noticeable role at low temperatures. At high temperatures, on the other hand, at which the doping by the usual methods is carried out the free energy of the crystal[8] G = H − TS becomes minimal because of the

entropy term, namely when a large number of vacancies is produced and electrons are exchanged between them and the impurity centers. This is why these centers are strongly compensated.

Ion doping, however, produces undesirable radiation defects, due to the transfer of a fraction of the crystal-lattice atoms from the sites to the interstices. This necessitates a subsequent annealing, whereby the radiation defects are eliminated and the atoms of the introduced impurities occupy in the crystal lattice a position in which they acquire the required electric activity. Experience shows that in many cases it is possible to choose annealing regimes in which the compensation is negligible.

A p-type layer (resistivity $\sim 10^4$ Ω-cm) was obtained in[59-61] by bombarding insulating ZnS crystals by silver ions, followed by annealing at $\approx 450°C$ in sulfur and ZnS vapor. Silver was chosen because the acceptor centers it produces in ZnS are stable[54] and have a relatively low ionization energy and good luminescent properties.

Approximately the same annealing temperature was used to produce p-n junctions of CdS doped with phosphorus[62,63], nitrogen[64], and bismuth ions[65]. The choice of acceptor impurities in the case of CdS, in our opinion, was determined by the possibilities of using the commercial ion-doping installations designed for silicon. From the point of view of acceptor properties, these impurities are far from being the best for II-VI compounds. The depths of the phosphorus and nitrogen acceptor levels in CdS are quite large (≈ 1 eV), so that it is impossible to obtain a low-resistance p-type region. Nonetheless, the obtained p-n junctions produced yellow and even green electroluminescence at a forward current ≈ 10 mA.

The first report of successful change of the type of conductivity in the highly-conducting ZnSe (n-type) is contained in[66]. The type of conductivity was changed by introducing lithium ions (acceptor impurity) followed by annealing at 300—400°C. The diodes obtained from these samples produced yellow electroluminescence at a current 0.07 mA.

Concluding the discussion of the prospects of the ion-doping method as applied to II-VI compounds, we note that the obstacle to thermodiffusion or any other high-temperature method of doping is in many cases the relatively low volume solubility of the acceptor and donor impurities. As a result, the introduced impurity settles on the surface or decorates dislocations, forming a second phase. The ion-doping method in which the diffusion processes that determine precipitation of a second phase do not play a noticeable role (since the temperature is low) makes it possible to raise significantly the solubility limit. This is of particular importance because of the relatively large ionization energy of the impurity centers, especially acceptors, in II-VI compounds.

Another method of producing injection light sources is to prepare heterostructures, particularly heterojunctions[9]. In principle this makes it possible to avoid the difficulties connected with the tendency of wide-band II-VI semiconductors to acquire one type of conductivity. As seen from Table II, in most cases we have at our disposal material of the n-type. It is therefore necessary to ensure injection of holes into this material.

TABLE II

Semi-conductor	Type of crystal lattice	Crystal lattice constants	Type of conductivity	Work function Φ, eV [²]	θ *),eV [²]
ZnS	Cubic	$a = 5.41$ 67	n-type	5.4	7.5
	Hexagonal	$a = 3.81, c = 6.23$ 68			
ZnO	»	$a = 3.24, c = 5.19$ 68	»	4.68	7.82
ZnSe	Cubic	5.65 67	»	4.84	6.82
ZnTe	»	6.07 67	p-type	5.43	5.76
CdS	Hexagonal	$a = 4.13, c = 6.69$ 68	n-type	5.01	7.26
CdSe	»	$a = 4.30, c = 7.02$ 68	»	5.22	6.62
CdTe	Cubic	6.41 67	n-, p-type	4.67	5.78

*Energy distance from the top of the valence band to the vacuum level.
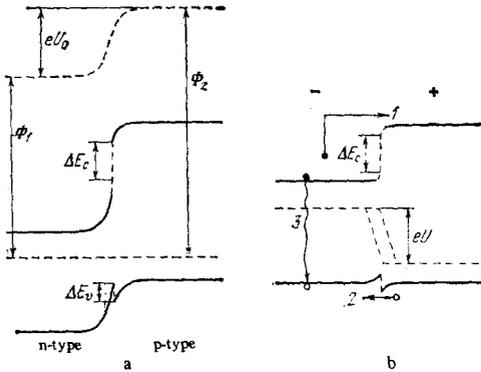

FIG. 4. Idealized band scheme of heterojunction: a) at equilibrium; b) with the voltage U applied in the forward direction. Φ_1 and Φ_2 —work functions of the semiconductors of n- and p-type, respectively; ΔE_c—energy gap in conduction band; ΔE_v—energy gap in valence band; 1—electron extraction; 2—hole injection; 3—radiative electron-hole recombination.

This means that to prepare a heterojunction it is necessary to have semiconducting material of p-type, which must be crystallographically compatible with the luminescent material, i.e., it should have a similar structure in approximately equal lattice constants. In addition, it should have a large work function and a larger forbidden band, or at least one of nearly equal width (Table II).

Crystallographic compatibility is essential in order for the lattices to grow together and in order to decrease the number of interface electronic states. These states correspond to centers of rapid nonradiative recombination, which participate in the so-called tunnel-recombination mechanism of current flow through a heterojunction.[69,70].

The large work function and the wide forbidden bands are needed in order that the extraction of the electrons from the luminescent semiconductor not prevail over the injection of holes into the semiconductor (Fig. 4).

Many attempts were made to develop heterojunctions based on wide-band II-VI semiconductors. So far, however, no material having all the aforementioned properties has been found. As a result, one of the main advantages of II-VI semiconductors was lost, namely the large probability of radiative recombination. This was due to the formation fast-nonradiative-recombination centers on the boundary of the two phases. In addition, the effectiveness of the heterojunctions was strongly lowered because extraction of the majority carrier from the luminescent semiconductor prevailed over the injection of minority carriers into it. It is possible that a way out of this situation will be found by producing a smooth variation of the solid solution of the n-type

FIG. 5. Band scheme of a contact between a metal and an n-type semiconductor with an inversion layer: a) at equilibrium; b) with voltage applied in the forward direction. I—n-region, II—inversion layer; E_F—Fermi level; E_0—center of forbidden band of semiconductor; •—free electron, o—free hole; "—"—luminescence center; $\ominus$—ionized luminescence center. 1—electron extraction; 2—hole injection; 3—interband radiative electron-hole recombination; 4—radiative recombination on luminescence centers.
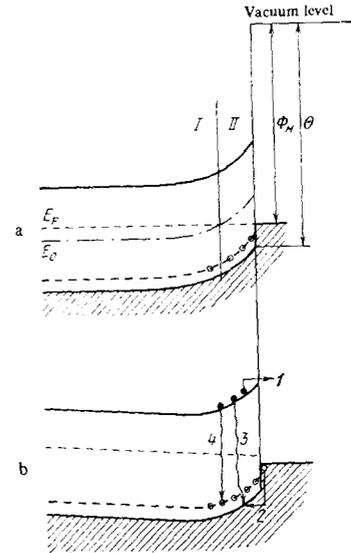
semiconductor with the p-type semiconductor, resulting in a continuous p-n heterojunction without a phase boundary with nonradiative centers. To this end it is necessary that both semiconducting compounds produce an extensive series of solid solutions. It appears that smooth heterojunctions were produced in the $Zn_xCd_{1-x}Te$ solid solution in the vicinity of $x = 0.4$[71]. The external electroluminescence quantum yield is 6% at 77°K. The emission maximum is located near 720 nm.

Minority carriers can also be injected into the semiconductor from a metallic contact. To this end, the metal must have a suitable work function (larger than that of the n-type semiconductor and smaller than that of the p-type). In this case, too, the competing process is the extraction of the majority carriers.

Somewhat better conditions for radiative recombination, to the detriment of extraction, are realized when an inversion layer, i.e., a layer with reverse type of conductivity, is produced in the semiconductor region near the contact. Such a layer is produced when the bending of the semiconducting bands near the contact is so large that the Fermi level turns out to be in the other half of the forbidden band.

Figure 5 shows the band scheme of an n-type semiconductor in contact with a metal having a larger work function. As is seen from the figure, the luminescence centers in the inversion layer are partially ionized (filled with holes)[10] already when the barrier is formed. The necessary condition for the formation of the inversion layer in the case of an n-type semiconductor (see Fig. 5) is the relation $\Phi_M \geq \Theta - (E_g/2)$, where Φ_M is the work function of the metal and Θ is the energy distance from the top of the valence band to the vacuum level. The inverse inequality, $\Phi_M \lesssim \Theta - (E_g/2)$, holds for p-type semiconductors.

Actually, the conditions for effective injection are even more stringent, namely $\Phi_M \geq \Theta$ (n-type) and $\Phi_M \leq \Theta - E_g$ (p type). Under these conditions, the edges of the corresponding bands (the top of the valence band in n-type semiconductors and the bottom of the conduction band in p-type semiconductors) bend at the contact in such a way that they reach or cross the Fermi level. This means that a degenerate state is produced in the inversion layer.

Unfortunately, it is impossible to realize these conditions in most wide-band II-VI semiconductors of n-type[13]. By way of example let us consider ZnS. Using the data given in Tables I and II, let us determine the work function that the metal must have to produce an inversion layer. We obtain $\Phi_M \geq 5.65$ eV. The metal with the largest work function is platinum, with $\Phi_{Pt} \approx 4.7$ eV[73]. We see that even this value is small for ZnS.

However, an inversion layer can be produced also by contact with a chemical compound having the necessary work function.

Low-voltage electroluminescence of ZnS as a result of the formation of an inversion layer was observed in[74]. This layer was produced at a contact of ZnS with concentrated sulfuric acid. Blue luminescence was observed at a direct current 0.27 mA (voltage 12 V). The quantum yield was ~0.01%.

In a number of studies they used instead of the "metal-semiconductor" structure more complicated heterostructures, namely "metal-insulator-semiconductor." The introduction of the insulator makes it possible in some cases to use metals whose work function does not satisfy the condition for the formation of the inversion layer. The forbidden band of the insulator used in such a structure should be so placed relative to the vacuum level that an additional potential barrier is produced and hinders the extraction of the majority carriers of the semiconductor, but no barrier interfering with the injection of the minority carriers should be formed. It is customary to use wide-band oxides for this purpose. The first such electroluminescent device was constructed in[75].

However, the electroluminescence efficiency of complex heterostructures is low. The probable reason is that it is difficult to avoid nonradiative recombination via interphase states on the boundary between the semiconductor and the insulator.

Thus, the most promising for injection light sources based on wide-band II-VI semiconductors are p-n junctions obtained by the ion-doping method, as well as continuous heterojunctions based on solid solutions with variable composition.

In concluding this section, let us consider "low-voltage" pre-breakdown electroluminescence. It is produced when a relatively low voltage is applied to the sample and is concentrated in such a thin semiconductor layer that a near-breakdown field is produced in this layer. The electric-breakdown processes cause ionization of the crystal lattice and of the luminescence centers. Such an electroluminescence can arise, for example, in the barrier of an inverse-biased p-n junction, in a mobile electronic domain[12], and obviously in a thin single-crystal layer.

Pre-breakdown electroluminescence of p-n junction in ZnS was observed in[54]. At a voltage 25 V, a large fraction of the luminescence corresponded to interband recombination of electron-hole pairs (≈ 335 nm).

Mobile electronic domains are produced in crystals with relatively low resistivity. In[77,81] there was observed low-voltage luminescence of ZnS crystals of resistivity ~10^4 Ω-cm, due to concentration of the electric voltage in an acoustoelectric domain[13]. The luminescence region moved over the crystal together with

the domain, at acoustic velocity. The luminescence, including blue and ultraviolet emission, was observed in a sample ≈ 1 mm thick at ≈ 20 V. The energy efficiency was ~10^{-3}%. The inertia delay was $\lesssim 2 \times 10^{-7}$ sec, which is smaller by 3–4 orders of magnitude than in the case of powdered electroluminors based on ZnS. "Domain" electroluminescence can apparently find application in devices with optical scanning and also in pulsed light sources.

As to thin single-crystal layers, a remarkable result was recently obtained with sublimated ZnS films, namely a transition from pre-breakdown electroluminescence to the stimulated emission regime, i.e., the laser effect was produced in electric breakdown of the semiconductor[82].

3) Light receivers. The production of p-n junctions and heterojunctions in wide-band semiconductors of the II-VI group is important for the construction not only of sources but also of receivers for short-wave light, based on the photovoltaic effect in the potential barrier of the p-n junction. The generated emf's can reach values equal to these barriers. Thus, for example, a photo-emf ≈ 2.5 V was obtained with p-n junctions in ZnS[54]. The higher conversion efficiency of the optical energy into electricity, attained in solar batteries based on the heterojunction $CdTe - Cu_2Te$, amounts to ≈ 7.5% ($300°$ K)[83-85]. Anomalously high photo-emf's, reaching hundreds of volts, were observed in certain ZnS crystals[86-88]. This was due to the summation of emf's in a large number of barriers connected with stacking faults. The powers generated, however, were negligibly small.

Let us return to "poor" p-n junctions obtained by usual methods, for example by thermodiffusion of the impurity, but now in connection with the problem of the so-called photo-p-n-junction. Both the n and the p region in these p-n junctions are strongly compensated. This means that the electrons in the p region have moved away from the compensating donors to the acceptors, converting these donors by the same token into electron traps, while in the n region the electrons have moved from most donors to compensating acceptors, converting the latter into hole traps. When such p-n junctions are illuminated with light corresponding to the intrinsic absorption of the semiconductor, free electrons and holes are generated in the n and p regions. If the traps and the compensated donors and acceptors have suitable properties, a situation may arise wherein the electrons in the p region are captured by the traps and the holes remain free, and conversely, the holes in the n region are captured by the traps while the electrons remain free. The resistance of either the n or the p region is then greatly decreased because of the increase in the density of the majority carriers, and a good p-n junction state is obtained. A p-n junction with this property is called a photo-p-n junction. When it is illuminated, it is obvious that not only the direct current, but also the injection luminescence can increase in this junction. Either one can be used to record the initiating light. A similar phenomenon can be observed also in "frozen" p-n junctions, in which the donors and acceptors are deep (on the order of several tenths of an electron volt), so that illumination with appropriate infrared light is necessary to free the electrons in the end region and the holes in the p region. A p-n junction having these

properties was realized on the basis of $Zn\ Se_xTe_{1-x}$[89]. The quantum yield of the injection electroluminescence at $70°K$ reaches $\approx 20\%$.

We shall not dwell in detail on the photoconductivity. It has been the subject of many articles and monographs (see, e.g.,[90-97]). The electric and optical properties of semiconductors based on II-VI compounds are under intense investigation even now. They are of interest not only because of the abundance of physical effects, but also because of the prospects of their practical utilization. A high photosensitivity could be obtained in all the compounds of this group; the range of forbidden-band widths, as already noted, makes it possible to obtain maximum photosensitivity starting with the near ultraviolet all the way to the near infrared region of the spectrum. Interest in these photoconductors has increased recently in connection with a number of optoelectronic problems, such as the development of high-efficiency light receivers, operative-memory cells, modulating and scanning devices, active elements for amplifiers and converters of light and images, radiation converters and controllable transparencies, etc. The photoconductivity phenomena are observed in an unusually wide range—photocurrents are observed in materials having resistivities from 1 to $10^{18}\ \Omega$-cm. The free-carrier lifetime, which determines the photosensitivity of the material, ranges from dozens of minutes to 10^{-12} sec.

It is known that the most widely used semiconductors of the II-VI groups are photoconductors based on CdSn and CdSe. Much progress was made both in the understanding of the processes that occur in them, principally as a result of the work by Bube and Sheinkman (see, e.g.[90 93-97]), and in the receiver technology, where much was done by Dolomiets (see, e.g.,[98]). It was established that the photosensitivity of materials with suitable band structure is determined mainly by the so-called r-centers[93,96]. In n-type semiconductors, these are compensated singly-charged acceptors, hole traps[14], which are in many cases also the luminescence centers. They usually represent intrinsic defects of the crystal lattice or else complexes comprising an intrinsic defect and an impurity. The main parameter limiting the application of such receivers is their high inertia at low illuminations. Thus, for example, the smallest inertia of the photoreceivers in image amplifiers amounts to ≈ 20 msec in the case of CdS and 1 msec in the case of CdSe. It should be noted once more that, according to statements made by staff members of the Siemens concern (West Germany) the inertia of photoreceivers based on ZnO is much lower than in the case of CeS and CdSe.

One of the interesting phenomena observed in many photosemiconductors is infrared quenching of photoconductivity. This is one of the most important phenomena with the aid of which wide-band semiconductors can be used to register infrared light. It was observed by a number of workers in various photosemiconductors, including CdS, CdSe[90,93-97], ZnSe[99,100] and ZnS[101]. It was investigated theoretically most completely by Kalashnikov, Maev, and Pustovoit (see, e.g.,[102]). The gist of this phenomenon is that the photocurrent, or equivalently the concentration of the nonequilibrium carriers, in a photosemiconducting crystal illuminated by infrared light of definite wavelength can decrease abruptly, by four or five orders of magnitude, thereby essentially
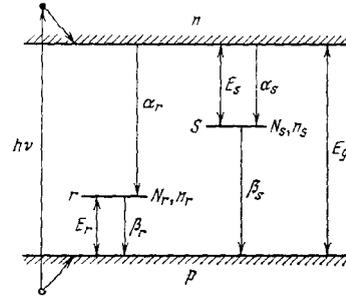

FIG. 6. Energy level scheme of photosemiconductor with two types of centers electron capture probabilities by the corresponding centers, r and S. E_r, E_S—positions of energy levels of centers; N_r, N_S—their concentrations; n_r, n_S—concentrations of the electrons on them; α_r, α_S—electron capture probabilities; β_r, β_S—hole capture probabilities. The directions of the straight arrows correspond to electron transitions. ●—free electrons, o—free holes (the wavy arrows indicate thermalization processes).

transferring the crystal from the state of a normal semiconductor into the state of a good insulator. The nature of the occurring phenomena can be explained by considering the band scheme of an n-type photoconductor with two types of centers (Fig. 6). These are, first, the r centers and second the so-called S centers, which are centers of rapid and as a rule nonradiative recombination of electron-hole pairs. The nature of these centers is not yet fully clear, but these centers are registered by investigating the kinetics of the photoconductivity. The levels corresponding to these centers lie closer to the center of the forbidden band, and the probabilities of electron and hole capture by these centers, α_S and β_S, are approximately of the same order and lie in the range $\sim 10^{-8}$—$10^{-10}\ cm^3\ sec^{-1}$, depending on the particular properties of the material. For our centers we have $\beta_r/\alpha_r \sim 10^4$—$10^6$, $\alpha_r \sim 10^{-10}$—$10^{-13}\ cm^3\ sec^{-1}$[95,96]. When such a semiconductor is illuminated with light having a quantum energy $\hbar\omega \geq E_g$, electrons and holes are generated in the conduction and valence bands, respectively. In the presence of r centers, the holes from the valence band are captured mainly by the r centers and the channel of recombination via the S centers has low effectiveness, so that ordinary photoconductivity is observed. When infrared illumination with a quantum energy on the order of the depth of the hole trap (r center) is applied, the holes leave these centers. The growth of the hole concentration in the valence band leads to an increase in the channel of electron recombination via S centers, and consequently to a sharp drop of the electric conductivity of the sample. Experiment shows that this drop can reach five or six orders of magnitude[98,99]. It appears that this phenomenon is nearly as effective as the intrinsic photoconductivity, but has less inertia. As shown by theoretical estimates[103], the relaxation time can be approximately 10^{-6}—10^{-8} sec. An analysis of the kinetics of the processes that occur within the framework of such a two-level model (see the band scheme in Fig. 6) enables us to formulate the necessary conditions that must be satisfied by the center parameters in order for the infrared excitation of the photoconductivity to become effectively manifest[102]. First, the concentration of the free carriers in the conduction band should be lower than the concentration of the r centers. This relation makes it possible to modify significantly, with the aid of the r centers, the concentration of the free electrons in the conduction band. Second, $\alpha_r/\alpha_S \ll \beta_r/\beta_S$. Satisfaction of this condition ensures an appreciable differ-

ence between the r and S centers and makes it possible to accumulate holes at the r centers (i.e., to sensitize the crystal). Third, $n_r \beta_r > n_S \beta_S$. This condition ensures a larger and overwhelming activity of the r centers with respect to hole capture. It must be emphasized that infrared extinction of photoconductivity is observed most frequently in crystals with high photosensitivity, so that in the preparation of the corresponding materials one should bear in mind the joint occurrence of these phenomena.

4) Devices for light-beam control and laser technology. Semiconductor materials of the II-VI group are widely used in devices connected with control of optical signals.

There are many processes of variation of absorption, refraction, and diffraction scattering of light, which lead to modulation and deflection (scanning) of laser beams[104-107]. Nevertheless extensive research is being carried out on new materials and physical phenomena capable of increasing the efficiency and expanding the spectral range over which the optical signal can be controlled. It becomes obvious that the use of semiconducting materials is particularly promising for optical frequencies close to the fundamental absorption edge. To modulate this light, extensive use is made of the Franz-Keldysh effect (shift of the intrinsic absorption energy by an electric field); see, e.g.,[104].

For optoelectronics problems, at the same frequencies, interest attaches to infrared extinction of photoconductivity. The point is that the dielectric constant, and consequently also the refractive index, depend essentially on the concentration of the electrons in the conduction band. Infrared extinction of the photoconductivity makes it possible to vary the number of electrons in the conduction band and to control the refractive index of the semiconductor. A theoretical analysis of this effect[108] has shown that it is possible to vary the dielectric constant, particularly in CdS, by as much as several tenths of 1%.

The light beam is effectively modulated by rotating the plane of polarization as a result of the electrooptical effect. The linear electrooptical effect (the Pockels effect) of ZnTe and CdTe exceeds by several times the corresponding coefficient of GaAs. Its value varies little in a wide spectral region.

For modulation and scanning of light one can use the diffraction of light by ultrasonic waves in crystals. For optical frequencies close to the intrinsic absorption edge, specific mechanisms of elastic optical interaction become significant. In this case the propagation of an acoustic wave in a crystal leads to periodic modulation of both the width of the forbidden band (via the deformation potential) and of the electron density in the conduction band[109]. The latter mechanism is important for piezosemiconductors. In all probability it is precisely these two processes that cause effective modulation of the light flux by moving acoustoelectric domains in CdS crystals[110-112] at frequencies corresponding to the intrinsic absorption edge.

Naturally, for a practical realization of all these effects it is necessary to have crystals in which the impurity absorption does not "smear out" the intrinsic absorption edge. To broaden the spectral range of devices used to control optical signals it is necessary also to have a large assortment of mixed crystals.

Semiconducting materials of the II-VI groups are widely used in laser technology. They are successfully used as optical media for lasers in the visible and ultraviolet bands with two-photon optical pumping (see Brodin's monograph[113] 15).

Crystals having a structure without an inversion center, for example ZnTe, are used as nonlinear optical elements to generate laser harmonics (to increase the laser frequency), and also to obtain difference frequencies (generation of submillimeter wavelengths)[114]. By using wide-band II-VI semiconductors it is possible to vary laser parameters in a wide range.

In[115] it is proposed to use nonlinear absorption of crystals, for example two-photon absorption, to vary the laser-emission duration from 20 nsec to 1 μsec. To this end, a crystal with two-photon absorption must be placed inside the resonator of a Q-switched laser. This produces inertialess negative feedback. The limitation of the light flux in crystals with two-photon absorption causes not only a change in the duration of the light pulse, but also an improvement in the spatial structure of the beam[116].

Lasers with variable pulse duration were already produced by using CdS nonlinear elements (in ruby lasers[115-117]) or CdSe (in neodymium lasers[116,118]).

Lasers of this kind can be used as heterodyne-lasers. They can be used to pump parametric light generators (in which case a stationary operating regime is possible)[119] and to study the kinetics of chemical, biological, and physical processes.

Two-photon absorption of CdS, $CdS_x Se_{1-x}$, CdSe, and ZnS is used to limit the intensity of laser beams[120,121].

The use of crystals with two-photon absorption CdS, ZnS, $CdS_x Se_{1-x}$) is also promising for the measurement of certain parameters of ultrashort light pulses. Thus, for example, the absolute values of the first moments of mode-locked neodymium-laser emission were measured in[122,123] by using nonlinear absorption of light by $CdS_x Se_{1-x}$ single crystals in two-photon interband transitions, which leads to an exponential decrease of the pump-radiation intensity. $CdS_x Se_{1-x}$ and ZnS crystals were used to determine the pulse duration of the fundamental and doubled frequency (~10^{-12} sec) of a mode-locked laser. This method is based on measuring the emission region produced as a result of two-photon absorption by the crystal when f pulsed light beams overlap[124]. The use of semiconductors for this purpose instead of liquid dyes offers many advantages, due to the high probability of two-photon absorption and to the larger luminescence quantum yield due to this absorption. This makes it possible to measure the duration of the light pulses at relatively low light-flux intensity. For the same reason it is possible to increase also the time resolution of the method, since one can use objectives with smaller aperture[125]. An important role is played also by the possibility of selecting the two-photon absorption of a semiconductor with suitable forbidden-band width to investigate lasers with different emission wavelengths. Owing to the use of mixed crystals, this selection is simpler than the selection of a suitable dye.

Crystals used in laser technology must obviously have the high homogeneity and purity usually required of laser materials.

b) **Elements for acoustoelectronics.** The last decade has seen a vigorous development of another new branch of science and technology, namely acoustoelectronics. This trend is based on the following phenomenon, first observed in CdS: If the semiconductor is subjected to an electric field such that the electron or hole moves in it with velocity larger than the phase velocity v_S of the acoustic waves, then amplification and generation of acoustic waves takes place in the crystal[126,127].

The physical process that occurs upon amplification and generation of acoustic waves by a drifting flux of electrons in a solid consists in the following: The passing elastic wave leads to a redistribution of the electrons in space in such a way that the region with increased electron density is produced, i.e., a volume space charge. If the space charge is now made to drift by an external and electric field in the wave direction with supersonic velocity, then the space charge will emit phonons, in analogy with free electrons.

This is the nature of the amplification effect at low frequencies, when the amplification or generation of the elastic waves are due to Cerenkov radiation of the space charge produced by the wave itself. At high frequencies, when no space charge can be produced within a time equal to the period of the wave, the amplification of the acoustic waves is due to the Cerenkov radiation of the individual electrons, in analogy with the two-stream instability in a gas-discharge plasma.

It is important that the experimentally obtained signal gains are large enough (10^2-10^3 dB/cm), and that this phenomenon can be widely used in technology (see, for example, the reviews[128,129]).

The functional connection between the individual elements in acoustoelectronic devices is realized with the aid of acoustic waves.

At the present time, many different models of instruments based on this phenomenon have been proposed. They cannot be described in a brief review, and we therefore shall dwell only on the principal elements of acoustoelectric devices; all these devices can be obtained by combining and elaborating these fundamental elements.

1) _Amplifiers of acoustic and microwave oscillations, active delay lines._ The schematic diagram of an acoustoelectric amplifier is shown in Fig. 7[126,128]. An electric microwave signal from the generator is fed to a converter, which transforms an electric microwave signal into an acoustic signal, i.e., into a propagating acoustic wave. The sound wave then passes through the first buffer into the active medium of the amplifier, which is a piezosemiconducting crystal, is amplified in this crystal and then, passing through a second buffer, enters a second converter in which the acoustic signal is transformed into an electric microwave signal detected by a receiver. The converters can be CdS, CdSe, or ZnO piezoelectric crystals or films[130]. The buffers are simply passive media for the acoustic waves and isolate electrically the power supply of the active element from the generator and the receiver. It is important that all the elements of the acoustoelectric amplifier can be made from II-VI compounds. The most actively used active media are CdS, CdSe, and ZnO crystals (the latter is the most promising). In these crystals, a voltage source is used to produce an electric field that causes a directional drift of electrons
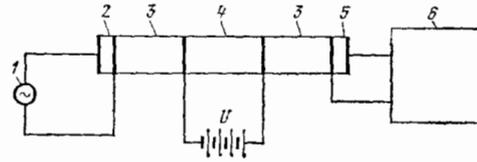

FIG. 7. Schematic diagram of acoustoelectric amplifier: 1—generator of microwave electric oscillation; 2, 5—piezoelectric signal converter; 3—buffer, 4—piezosemiconducting crystal (active medium); 6—microwave signal receiver; U—power supply.

with velocity larger than the phase velocity of the sound wave. The gain in crystal is $K = \exp(\gamma L)$ where L is the crystal length and γ is the gain increment per unit crystal length. Values $K \sim 10^3-10^6$ have been attained in CdS and CdSe.

In the simplest case[128] we have

$$\gamma = -\frac{1}{2}\xi^2 \frac{4\pi\sigma_0}{v_s\varepsilon_0} \frac{1-(v_d/v_s)}{[1-(v_d/v_s)]^2+(4\pi\sigma_0/\varepsilon_0\omega)^2(1+q^2r_D^2)^2},$$

where ξ is the electromechanical coupling constant or the constant of interaction between the electrons and the phonons. It is determined by the value of the piezo-effect in the crystal: $\xi^2 = 4\pi\eta^2/\rho v_S^2\epsilon_0$, where η is the piezoelectric constant (for acoustic waves with given polarization and along a given propagation direction), ρ is the density of the crystal, ϵ_0 is the (lattice) dielectric constant of the crystal, σ_0 is the conductivity, q is the wave number of the acoustic wave, r_D is the Debye radius, and v_d/v_s is the ratio of the drift velocity to the sound velocity. It is seen that amplification takes place only if the condition $v_d > v_s$ is satisfied. This is a necessary condition and at the same time very difficult to satisfy. Indeed, since $v_d = \mu\mathscr{E}$, where μ is the mobility and $\mathscr{E}$ is the electric field, this condition leads in final analysis to contradictory requirements that the crystal have a maximum mobility and a sufficiently large electron-phonon interaction constant ξ. We recall that the larger ξ the stronger the scattering of the electrons by the phonons and the lower the mobility μ.

Acoustoelectronic signal amplifiers are usually somewhat inferior to transistor amplifiers from the point of view of gain, and have a more complicated technology. The acoustoelectronic amplifier, however, has one very important practical feature—besides amplifying the microwave signal it introduces a large signal time delay, since the velocity of sound is much less than that of the electromagnetic waves. It is possible to obtain a delay time $\sim 10-100$ μsec. Such delay lines are very important for practical applications in radar, computer technology, and navigation and remote-control systems, in airborne apparatus, etc.[131].

Investigations carried out principally on CdS and CdSe have shown that one of the main obstacles to obtaining high gains is the inhomogeneity of the samples. This may be either the technological inhomogeneity of the crystal or an inherent inhomogeneity due to the uneven distribution of the electric field in the amplification regime, due to the reaction of the growing acoustic oscillations on the stationary state of the semiconductor plasma. As a result only a small part of the sample amplifies the acoustic oscillations effectively.

To prepare active delay lines it is necessary to have homogeneous crystals with a linear dimension $\sim 1-10$ cm.
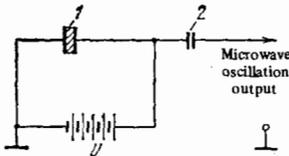
FIG. 8. Schematic diagram of acoustoelectric microwave generator: 1—semiconductor crystal or single-crystal film; 2—decoupling capacitor; U = power supply.
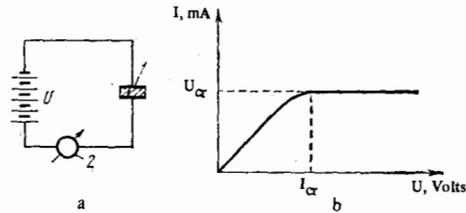

FIG. 9. Schematic diagram of acoustoelectric device with stationary phonon flux (a) and its current-voltage characteristic (b). 1—Piezosemiconducting crystal; 2—current meter; U—power supply; U_{cr} and I_{cr}—threshold voltage and saturation current, respectively.

2) Generators of acoustic and microwave oscillations and other devices based phonon-generation effect. If only one electric field is applied to a piezoelectric semiconductor crystal, then spontaneous phonon generation in the crystal sets in. When the dimensions of the crystals are limited and commensurate with the wavelength of the generated acoustic noise (sublimated film or thin plate), then acoustic and microwave oscillations with narrow generation band are produced in the semiconductor. Devices of this kind (Fig. 8) can be used as small-size acoustic or microwave generators with very narrow generation band. For example, at $f = 600-700$ MHz the line width is $\Delta f \sim 10$ kHz. The line is so narrow because this system is in essence an active acoustic resonator[132].

If the crystal dimensions greatly exceed the wavelength of the generated acoustic noise, then the growing phonon flux leads to an abrupt change in the behavior of the crystal in an external electric field. Two cases are possible here—the phonon flux can be stationary or nonstationary in time.

The first case is characterized by a stationary phonon distribution. With increasing voltage, a static acoustolectric domain is produced near the anode and the ohmic section on the current-voltage characteristic changes abruptly into a current-saturation section (Fig. 9). This current saturation is usually called Smith saturation[133]. This phenomenon is used in semiconducting current stabilizers.

As to the nonstationary phonon flux, it is this flux which causes the already mentioned moving acoustoelectric domain in the crystal. The velocity of domain motion through the crystal is equal to the sound velocity. At the instant when the domain leaves the crystal, a current surge is produced in the electric circuit. The current density in the sample with the domain usually satisfies the relation $j = env_s$, where e is the electron charge and n is the free-electron density. This is connected with the fact that the electrons are trapped in potential wells inside the domain by the sound wave, and therefore the electron drift velocity is equal to the wave velocity.

Let now the electron concentration vary along the crystal (along the coordinate x), say as a result of a change in the illumination. In other words, the electron density distribution is given by $n = n(x)$. It is then ob-

vious that the current I in the circuit will have a time dependence $I(t) = en(x)v_s$, where $x = v_st$, i.e., the plot of the current against the time t is a duplicate of the plot of the density against the coordinate x. This principle can serve as a basis for shaping current pulses of arbitrary profile and, in addition, for "reading" optical images, i.e., conversion of optical images into electric pulses[134]. In this case the materials must have high photosensitivity and homogeneity. The most suitable materials are CdS, CdSe, and ZnO, which are the most photosensitive.

c) Ionizing-radiation detectors. Significant changes have occurred recently in the methods used for the registration and spectrometry of charged particles, owing to the use of semiconductor detectors based on germanium and silicon.

The charged particles are registered by these detectors because the conductivity of the latter is increased upon irradiation.

Semiconductor detectors (counters) for nuclear particles are solid-state ionization chambers in which the carriers produced by absorption of the radiation are gathered on electrodes. Semiconductor detectors can register any radiation capable of producing sufficient ionization in the sensitive layer. The higher the resistance of the sensitive layer, the smaller the ionization that can be registered, so that to detect radiation one uses high-resistance homogeneous crystals and inverse-biased p-n junctions.

Particularly good results were obtained in the registration and spectrometry of ionizing particles with short mean free paths (α and β particles, ions, and fission fragments).

Germanium detectors are used also in γ spectrometry, owing to their relatively high energy resolution. In this case the samples are made with a large sensitive region, ~ 10 cm³, usually obtained by introducing lithium ion under the influence of an electric field. A shortcoming of these detectors is that they must operate and even be stored at low temperatures. The small width of the germanium forbidden band precludes their operation at room temperature, and the high mobility of the lithium ions makes it necessary to store the samples at liquid-nitrogen temperature.

Further progress was made through the use of wide-band semiconductor materials. Detectors developed on the basis of CdTe could operate at temperatures up to $+100°C$[135].

The CdTe elements have a relatively large atomic number[16) Z, a factor of importance to the effective registration of γ radiation. It absorbs particularly effectively γ quanta of medium energy, when the absorption coefficient is determined by the photoeffect ($\kappa \sim Z^5$). The γ-quantum photoabsorption per unit volume of a CdTe detector is 4 and 50 times larger than in germanium and silicon detectors, respectively.

Counters based on CdTe can be used also to register thermal neutrons, particles that do not produce ionization directly. The point that when cadmium captures thermal neutrons γ radiation is produced, and the most intense spectral line has an energy 560 keV. It is the registration of this radiation which makes it possible to detect thermal neutrons. As shown by calculations[136] the efficiency with which thermal neutrons are

registered with CdTe detectors reaches $\approx 0.5\%$ at a sensitive-layer thickness ≈ 1 mm.

It should be noted once more that the grown CdTe crystals can be either p-type or n-type, and it is easy to prepare p-n junctions on their basis. This is important in some cases of detector production.

Some parameters of the CdTe counters cannot match as yet those of Ge or Si detectors, but come quite close to them. Thus, for example, the energy resolution has reached 32 keV for 5.5-MeV α particles[137] and 6 and 30 meV for γ quanta of 122 and 622 keV energy, respectively[138].

To register γ radiation in those cases when neither high energy resolution nor high speed is needed, one can use semiconductor detectors based on CdS and CdSe. It is important that capture of the holes by the traps can make the lifetime of the nonequilibrium electrons much larger than their time of flight between the electrons. As a result, internal amplification of the signal is produced and reaches $\sim 10^3-10^4$. Consequently, the current in high-resistance CdS single crystals irradiated by a Co[60] source at an intensity 1 R/hr increases to several microamperes under the operating conditions[139].

Work on improving detectors based on II-VI semiconductors should be aimed at decreasing their volume. Thus for example, measurements of the lifetime of the nonequilibrium carriers in CdTe show that it can reach $\sim 10^{-6}$ sec[138]; in this case the thickness of the working layer of the detector can be reduced to several millimeters.

To solve this problem one must obtain large homogeneous high-resistance crystals with high free-carrier mobility and with low trapping-center concentration.

Great practical interest attaches to the development of the commercial technology of detectors based on CdTe.

* * *

Thus, semiconducting materials based on wide-band II-VI compound have already found application in devices for optoelectronic, acoustoelectronics, and ionizing-radiation detection.

There is no doubt that advances in the technology will make it possible not only to improve the characteristics of the devices, but will also reveal new properties of these materials, of interest for practical use.

It is necessary at present to organized centralized commercial production of single-crystals and film structures of II-VI compounds, based on modern methods of synthesis, purification, doping, and control of semiconducting materials. This will result in considerable economy of efforts and means of the research centers, make the results of their investigations more comparable, and facilitate the task of developing a technology for high-grade devices with well-reproducible characteristics.

1) The table lists the best of the published mobility values.

2) We have in mind the emergence of the dislocations to the crystal surface when the latter is etched.

3) This remark pertains both to the efficiency and to the brightness of the electroluminescence.

4) Our model of this mechanism reduces approximately to the following: The electroluminor crystals contain (p)Cu₂S—(m)ZnS microheterojunctions. At a certain voltage (inverse bias) the Cu_2 S valence-band electrons become capable of tunneling into the ZnS conduction band (see Fig. 3), and of becoming effectively accelerated and ionized by impact of the crystal lattice and the defects, causing a cascade process. The high acceleration efficiency is due to the fact that the tunneling time is short in comparison with the polarization time of the crystal lattice; as a result, the electrons turn out to be free of the "heavy polar shirt." The primary and secondary electrons leaving the barrier are captured by the traps. Their return to the ionized luminescence center and the radiative recombination occur during the time when the polarity of the voltage is reversed; the release from the traps is effected then either by tunnel ionization or impact ionization, depending on the temperature. This is called pre-breakdown electroluminescence, since its excitation occurs as a result of electric breakdown processes that occur at a voltage insufficient for capacitor breakdown as a whole.

5) Domain electroluminescence will be discussed at the end of this section.

6) An exception is CdTe, on the basis of which p-n junctions were produced with an injection-electroluminescent efficiency 12% (77°K). The emission maximum occurs at 865 nm [48].

7) Introduction of impurities by bombardment with accelerated ions.

8) Here H is the enthalpy and S is the entropy.

9) p-n junctions in which the p and n regions consists of different semiconducting materials.

10) The luminescence centers in wide-band II-VI n-type semiconductors are usually compensated acceptors.

11) For p-ZnTe, the suitable metal for the production of the inversion layer is indium [72].

12) See, e.g., [76] concerning the nature of electronic domains.

13) Acoustoelectric domains will be discussed also in Sec. (b), devoted to acoustoelectronic elements, of this chapter.

14) These are compensated donors in p-n type photosemiconductors.

15) The use of II-VI compounds in electronically-pumped lasers was discussed in detail in a corresponding section.

16) $Z_{Cd} = 48$, $Z_{Te} = 52$, $Z_{Ge} = 32$, $Z_{Si} = 14$.

1 M. Cardona and G. Harbeke, Phys. Rev. A137, 1467 (1965).

2 R. K. Swank, ibid. 153, 844 (1967).

3 R. E. Nahory and H. Y. Fan, ibid. 156, 825.

4 J. C. Miklosz and R. G. Wheeler, ibid. 153, 913.

5 M. Cardona, J. Phys. Chem. Sol. 24, 1543 (1963).

6 E. Mollwo and R. Till, Zs. Phys. 216, 315 (1968).

7 D. T. F. Marple, J. Appl. Phys. 35, 1879 (1964).

8 R. E. Nahory and H. Y. Fan, Phys. Rev. Lett. 17, 251 (1966).

9 J. J. Hopfield and D. G. Thomas, Phys. Rev. 122, 35 (1961).

10 R. G. Wheeler and J. O. Dimmock, Bull. Am. Phys. Soc. 6, 146 (1961).

11 K. K. Kanazawa and F. C. Brown, Phys. Rev. A135, 1757 (1964).

12 R. E. Dietz, J. J. Hopfield, and D. G. Thomas, J. Appl. Phys. Suppl. 32, 2282 (1961).

13 M. Aven, D. T. F. Marple, and B. Segall, ibid., p. 2261.

14 M. Aven, J. Appl. Phys. 38, 4421 (1967).

15 R. G. Wheeler and J. O. Dimmock, Phys. Rev. 125, 1805 (1962).

16 F. Matossi, K. Lentwein, and G. Schmid, Zs. Naturforsch. 21a, 461 (1966).

17 M. Aven and W. Garwacki, Appl. Phys. Lett. 5, 160 (1964).

18 M. Aven and B. Segall, Phys. Rev. 130, 81 (1963).

19 A. G. Fischer, J. N. Carides, and J. Dresher, Sol. State Comm. 2, 157 (1964).

20 W. W. Piper and R. E. Halstead, Proc. of the Intern. Conference on Semiconductors, Prague, 1960, p. 1046.

[21] C. Cahali, F. Nava, G. Ottaviani, and C. Paorici, Sol. State Comm. 11, 105 (1972).

[22] C. Cahali, M. Martini, G. Ottaviani, and K. Zanio, Phys. Lett. A33, 241 (1970).

[23] J. A. Haanstra and J. Dielmann, Ext. Abstr. Meet. Electrochem. Soc. 14, 2 (1965).

[24] W. E. Spear and J. Mort, Proc. Phys. Soc. (Lnd.) 81, 130 (1963).

[25] C. Cahali, G. Ottaviani, and M. Martini, Appl. Phys. Lett. 19, 51 (1971).

[26] N. G. Basov, O. V. Bogdankevich, and A. G. Devyatkov, Zh. Eksp. Teor. Fiz. 47, 1588 (1964) [Sov. Phys.-JETP 20, 1067 (1965)].

[27] V. S. Vavilov, E. L. Nolle, and V. D. Egorov, Fiz. Tverd Tela 7, 746 (1965) [Sov. Phys.-Solid State 7, 596 (1965)].

[28] E. L. Nolle, V. S. Vavilov, G. P. Golubev, and V. S. Mashtakov, Fiz. Tverd. Tela 8, 286 (1966) [Sov. Phys.-Solid State 8, 236 (1966)].

[29] C. E. Hurwitz, Appl. Phys. Lett. 9, 116 (1966).

[30] O. V. Bogdanskevich, M. M. Zverev, A. I. Krasilnikov, and A. N. Pechenov, Phys. Stat. Sol. 19, K5 (1967).

[31] J. Bille, B. M. Kramer, P. Reimers, W. Ruppel, and R. Stille, ibid. 36, K71 (1969).

[32] N. G. Basov, O. V. Bogdankevich, V. M. Kamenev, V. P. Papusha, I. M. Pochernyaev, A. S. Nasibov, A. N. Pechenov, P. V. Shapkin, and V. I. Kozlovskiĭ, Dokl. Akad. Nauk SSSR 205, 72 (1972) [Sov. Phys.-Doklady 17, 685 (1973)].

[33] L. N. Kurbatov, G. S. Kozina, T. A. Kostinskaya, V. N. Favorin, and V. I. Gobatyrev, Radiotekhn. i élektron. 16, 637 (1971).

[34] N. G. Basov, O. V. Bogdankevich, and A. S. Nasibov, Inventor's Certificate, No. 270100, 1967. Otkrytiya, izobreteniya, promyshlennye obraztsy i tovarnye znaki (Discoveries, Inventions, Commercial Models, and Trade Marks), No. 16, 57 (1960).

[35] A. S. Nasibov, V. I. Kozlovskiĭ, and V. P. Papusha, Radiotekhn. i élektron. 18, 2151 (1973).

[36] O. V. Bogdankevich, A. S. Nasibov, A. A. Novikov, A. N. Pechenov, V. B. Fedorov, and V. V. Tsvetkov, Radiotekhn. i élektron. 16, 824 (1971).

[37] G. Destriau, J. Chem. Phys. 33, 620 (1936).

[38] W. W. Piper and F. E. Williams, Sol. State Phys. 6, 96 (1958).

[39] P. Zalm, Philips Res. Rept. 11, 353, 417 (1956).

[40] A. N. Georgobiani and M. V. Fock. Opt. spektr. 9, 775 (1960).

[41] A. N. Geogrobiani and M. V. Fock, ibid. 10, 188 (1961).

[42] A. N. Georgobiani, Tr. FIAN SSSR 23, 3 (1963).

[43] A. G. Fischer, J. Electrochem. Soc. 110, 733 (1963).

[44] I. K. Vereshchagin, Opt. spektr. 16, 290, 651 (1964).

[45] M. Yoshiyama, J. Kawarada, and T. Sato, Proc. of the 1970 IEEE Intern. Computer Group Conference, Washington, 1970, p. 261.

[46] H. Arai, T. Yoshizawa, K. Awazu, K. Kurahashi, and S. Ibuki, 1970 IEEE Conference on Display Devices, New York, 1970, p. 52.

[47] M. A. Weinstein, J. Opt. Soc. Am. 50, 597 (1960).

[48] G. Mandel and F. F. Morehead, Appl. Phys. Lett. 4, 143 (1964).

[49] F. Kröger, Chemistry of Imperfect Crystals, Wiley, 1964.

[50] A. M. Gurvich, Vvedenie v fizicheskuyu khimiyu kristallofosforov (Introduction to Physical Chemistry of Crystal Phosphors), Moscow, Vysshaya shkola, 1971.

[51] F. F. Morehead and B. L. Crowder, IBM J. Res. and Develop. 12, 458 (1968).

[52] A. N. Georgobiani and V. I. Steblin, Fiz. Tekh. Poluprovd. 1, 934 (1967) [Sov. Phys.-Semicond. 1, 775 (1967)].

[53] A. N. Georgobiani and V. I. Steblin, Zh. Prikl. Spektr. 7, 584 (1967).

[54] A. N. Georgobiani and V. I. Steblin, Tr. FIAN SSSR 50, 27 (1970).

[55] M. Aven, Appl. Phys. Lett. 7, 146 (1965).

[56] R. Yamamoto, M. Inoue, K. Itoh, and T. Shitaya, Japan J. Appl. Phys. 6, 537 (1967).

[57] R. Yamamoto and K. Itoh, ibid. 8, 341 (1969).

[58] R. Yamamoto, ibid., p. 890.

[59] A. N. Georgobiani and M. B. Kotlyarevskiĭ, Problemy fiziki soedinennii $A^{II}V^{VI}$ (Problems of Physics of II-VI Compounds), Vilnius State Univ. Press, 1972, p. 321.

[60] A. N. Georgobiani, M. B. Kotlyarevskiĭ, and Yu. P. Generalov, Kr. soobshch. fiz. (FIAN SSSR), No. 3, 17 (1972).

[61] A. N. Georgobiani, B. M. Kotljarevsky, V. N. Zlobin, P. A. Todua, Yu. P. Generalov, and B. P. Dement'ev, Mat. Res. Bull. 8, 893 (1973).

[62] W. W. Anderson and J. T. Mitchell, Appl. Phys. Lett. 12, 10 (1968).

[63] S. L. Hou and J. A. Marley, Appl. Phys. Lett. 16, 467 (1970).

[64] Y. Shiraki, T. Shimada, and K. Kamatsubara, J. Appl. Phys. 43, 710 (1972).

[65] F. Chernow, G. Eldridge, G. Ruse, and L. Wahlin, Appl. Phys. Lett. 12, 339 (1968).

[66] Y. S. Park and C. H. Chung, ibid. 18, 99 (1971).

[67] M. L. Cohen and T. Begstresser, Phys. Rev. 141, 789 (1966).

[68] G. B. Bokiĭ, Vvedenie v kristallokhimiu (Introduction to Crystal Chemistry), Moscow State Univ. Press, 1954.

[69] A. R. Riben and D. L. Teucht, Sol. State Electron. 9, 1055 (1966).

[70] A. R. Riben and D. L. Teucht, Intern. J. Electron. 20, 583 (1966).

[71] F. Morehead and G. Mandel, Appl. Phys. Lett. 5, 53 (1964).

[72] M. B. Miksic, G. Mandel, F. F. Morehead, A. A. Onton, and E. S. Schlig, Phys. Lett. 11, 202 (1964).

[73] E. V. Kulikova, I. V. Ryzhikov, and Yu. I. Sidorov, Élektronnaya tekhnika, ser. 2 (Poluprovodnikovye pribory) No. 3 (60), 3 (1971).

[74] L. J. Van-Ruyven and F. E. Williams, Phys. Rev. Lett. 16, 889 (1966).

[75] D. D. O'Sullivan and F. C. Malarkey, Appl. Phys. Lett. 6, 5 (1965).

[76] V. L. Bonch-Bruevich, I. P. Zvyagin, and A. G. Mironov, Domennaya elektricheskaya neustoĭchivost' (Domain Electric Instability), Nauka (1972).

[77] A. N. Georgobiani, A. V. Lavrov, P. A. Todua, and V. A. Chikhacheva, in: Élektrolyuminestsentsiya tverdykh tel (Electroluminescence of Solids), Naukova Dumka, 1971, p. 57.

[78] A. N. Georgobiani and P. A. Todua, Kr. soobshch. fiz. (FIAN SSSR), No. 5, 26 (1970).

[79] A. N. Georgobiani and P. A. Todua, ibid., No. 6, 28 (1971).

[80] A. N. Georgobiani, A. V. Lavrov, P. A. Todua, and V. A. Chikhacheva, ibid., p. 31.

[81] A. N. Georgobiani and P. A. Todua, J. Luminescence 5, 14 (1972).

[82] N. A. Vlasenko and Zh. A. Pukhliĭ, ZhETF Pis. Red. 14, 449 (1971) [JETP Lett. 14, 306 (1971)].

[83] R. W. Aldrich and D. A. Cusano, Research on Thin Film Polycrystalline Solar Cells, Techn. Rept. AFAPL-TR-65-8 (U.S. Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base), Ohio, 1965.

[84] D. A. Cusano, Sol. State Electron. 6, 217 (1963).

[85] D. A. Cusano and M. R. Lorenz, Sol. State Comm. 2, 125 (1964).

[86] S. G. Ellis, F. Herman, E. E. Loebner, W. J. Merz, C. W. Struck, and J. G. White, Phys. Rev. 109, 1860 (1958).

[87] G. Cheroff and S. P. Keller, ibid. 111, 98.

[88] W. J. Merz, Helv. Phys. Acta 31, 625 (1958).

[89] M. Aven and W. Garwacki, J. Appl. Phys. 36, 3202 (1967).

[90] R. H. Bube, Photoconductivity of Solids, Wiley, 1960.

[91] H. Levinstein, Photoconductivity, N. Y. Pergamon Press, 1962.

[92] S. M. Ryvkin, Fotoelektricheskie yavleniya v poluprovodnikakh (Photoelectric Phenomena in Semiconductors), Moscow, Fizmatgiz (1963).

[93] V. E. Lashkarev and M. K. Sheinkman, Phys. Stat. Sol. 11, 429 (1965).

[94] V. E. Lashkarev, M. K. Sheinkman, and I. B. Ermolovitch, II-VI Semiconductor Compounds Intern. Conference, New York, 1967.

[95] A. V. Lyubchenko and M. K. Sheĭnkman, see Ref. 59, Vol. 2, p. 34.

[96] A. Rose, Phys. Rev. 97, 322 (1955).

[97] A. Rose, Progr. Semicond. 2, 109 (1957).

[98] B. T. Kolomiets and A. O. Olesk, Élektrichestvo, No. 10, 71 (1962).

[99] A. Reinberg, W. Holton, M. de Wit, and R. Watts, Phys. Rev. B3, 410 (1971).

[100] H. Gobrecht, G. Gschwind, D. H. Haberland, H. Nelkowski, and A. Stais, Phys. Stat. Sol. a4, K19 (1971).

[101] C. Burget and C. Lin, J. Phys. Chem. Sol. 31, 1353 (1970).

[102] S. G. Kalashnikov, R. G. Maev, and V. I. Pustovoĭt, Fiz. Tekh. Poluprovdn. 5, 522 (1971) [Sov. Phys.-Semicond. 5, 456 (1971)].

[103] R. G. Maev, I. A. Poluektov, and V. I. Pustovoĭt, Fiz. Tverd. Tela 14, 2012 (1972) [Sov. Phys.-Solid State 14, 1738 (1973)].

[104] E. Mustel' and V. Parygin, Metody modulyatsii i skanirovaniya sveta (Methods of Modulation and Scanning of Light), Nauka (1970).

[105] D. Pinnow, IEEE Trans. Quantum Electron. QE-6, 223 (1970).

[106] R. Dixon, IEEE Trans. Electron. Dev. ED-17, 229 (1970).

[107] K. Tada and M. Aoki, Japan J. Appl. Phys. 10, 998 (1971).

[108] R. G. Maev, I. A. Poluéktov, and V. I. Pustovoĭt, Fiz. Tverd. Tela 15, 18 (1973) [Sov. Phys.-Solid State 15, 12 (1973)].

[109] V. M. Levin and R. G. Maev, ZhETF Pis. Red. 17, 127 (1973) [JETP Lett. 17, 90 (1973)].

[110] E. Kohn and M. Lampert, Phys. Rev. B4, 4479 (1971).

[111] K. Yamomoto, M. Yamada, and K. Abe, J. Appl. Phys. 41, 450 (1970).

[112] V. M. Levin and V. G. Maev, Trudy 8-ĭ Vsesoyuznoĭ akusticheskoĭ konferentsii (Proc. of Eighth All-Union Acoustic Conference), Moscow (1973).

[113] M. S. Brodin, in: Kvantovaya élektronika (Quantum Electronics), No. 5, Kiev (1971), p. 33.

[114] T. Yajima, and K. Inoue, Phys. Lett. A26, 281 (1968).

[115] J. Schwartz and C. S. Naiman, Appl. Phys. Lett. 11, 242 (1967).

[116] V. V. Arsen'ev, V. S. Dnepropetrovskiĭ, and D. N. Klyshko, Kvant. élektron. No. 1 (7), 33 (1972) [Sov. J. Quant. Electr. 2, 23 (1972)].

[117] J. Schwartz, W. Weiler, and R. K. Chang, IEEE J. Quantum Electron QE-6, 442 (1969).

[118] V. A. Aleshkevich, V. V. Arsen'ev, V. S. Dneprovskiĭ, D. N. Klyshko, and L. A. Sysoev, ZhETF Pis. Red. 9, 209 (1969). [JETP Lett. 9, 123 (1969)].

[119] S. A. Akhmanov and R. V. Khokhlov, Problemy nelineĭnoĭ optiki (Problems of Nonlinear Optics), Moscow, VINITI (1964).

[120] V. S. Dneprovskiĭ, D. N. Klyshko, and A. N. Penin, in: Nelineĭnaya optika (Nonlinear Optics), Novosibirsk, Nauka (1968), p. 83.

[121] V. V. Arsen'ev, V. S. Dneprovskiĭ, D. N. Klyshko, and A. N. Penin, Zh. Eksp. Teor. Fiz. 56, 760 (1969) [Sov. Phys.-JETP 29, 413 (1969)].

[122] V. V. Arsen'ev, V. S. Dneprovskiĭ, D. N. Klyshko, V. S. Fokin, and V. U. Khattatov, Zh. Eksp. Teor. Fiz. 63, 776 (1972) [Sov. Phys.-JETP 36, 407 (1973)].

[123] V. V. Arsen'ev, V. S. Dneprovskiĭ, D. N. Klyshko, and V. U. Khattatov, Kvant. elektron. No. 1 (7), 82 (1972) [Sov. J. Quant. Electr. 2, 81 (1972)].

[124] V. V. Arsen'ev, V. S. Dneprovskiĭ, D. N. Klyshko, and L. A. Sysoev, Zh. Eksp. Teor. Fiz. 60, 114 (1971) [Sov. Phys.-JETP 33, 64 (1971)].

[125] V. V. Korobkin and A. A. Malyutin, Kr. soobshch. fiz. (FIAN SSSR), No. 8, 53 (1970).

[126] A. R. Hutson, D. L. White, and J. H. McFee, Phys. Rev. Lett 7, 237 (1961).

[127] M. E. Gertsenshteĭn and V. I. Pustovoĭt, Radiotekhn. i élektron. 7, 1009 (1962).

[128] V. I. Pustovoĭt, Usp. Fiz. Nauk 97, 257 (1969) [Sov. Phys.-Uspekhi 12, 105 (1969)].

[129] A. Rose, RCA Rev. 27, 98 (1966); 28, 634 (1967); 32, 463 (1971).

[130] A. I. Morozov, V. V. Prokolov, B. A. Stankovskiĭ, and A. D. Gingis, P'ezopoluprovodnikovye prebrazovateli i ikh primenenie (Piezosemiconductor Converters and Their Application), Energiya (1073).

[131] G. Skino and T. M. Reeder, Microwave J. 13 (3), 79 (1970).

[132] J. D. Maines and E. G. S. Page, in: Trudy 9-ĭ Mezhdunarodnoĭ konferentsii po fizike poluprovodnikov (Proc. 9-th Internat. Conf. on Semiconductor Physics, Moscow, 1968) Leningrad, Nauka (1969), p. 983.

[133] R. W. Smith, Phys. Rev. Lett. 9, 87 (1962).

[134] A. Z. Dun and I. I. Troshkova, Obzory po elektronnoĭ tekhnike, ser. Élektronno-luchevye i fotoélektricheskie pribory (Reviews of Electronic Engineering, Series of Cathode-Ray and Photoelectric Devices), No. 4 (27), Moscow, NII Élektronika (1972).

[135] R. C. Beavin, Proc. of the Intern. Conference on CdTe, Strasbourg, 1971, Rept. 24.

[136] V. S. Vavilov, R. Kh. Vaganov, V. A. Chapnin, and M. V. Chukichev, Atom. Energ. 28, 505 (1970).

[137] A. Cornet, M. Hage-Act, and P. Siffert, Ref. 135, Rept. 26.

[138] K. Zanio, ibid., Rept. 21.

[139] J. F. Fowler, Phys. Med. and Biol. 8, 1 (1963).

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