SEMICONDUCTORS USED IN OPTOELECTRONIC
DEVICES - AN OVERVIEW

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Optoelectronic applications of semiconductors have been
growing rapidly. They comprise photodetectors, solar cells,
light emitting diodes and lasers. This article aims to
provide a general picture of the material aspect of these
devices. Emphasis is placed on material selection and
underlying reasons, as well as the state-of-the-art
performance.

Key words: photodetectors, solar cells, light emitting
diodes, semiconductor lasers, materials.

Introduction

    Semiconductor optoelectronics is defined as concerning
the transformation of light (within a wavelength range from
0.2μm to 0.2mm) into electrical energy in the form of
current flow through semiconductors and vice versa. It has
been for some years a very active field, both academically
and commercially. Its impact on equipment design is
increasingly felt, and the markets for optoelectronic
imaging systems as well as optical displays are growing
fast and healthily. In the laboratories, a great variety of
optical and optoelectronic measurement have become the

standard tools of the experimentalists and the applied
physicists in their investigation of conduction mechanisms
and energy band structures of semiconductors. As far as
large-scale technological exploitation is concerned, however,
the relevant optoelectronic effects are restricted to:
     Photoconductivity,
     Photovoltaic effect,
     Luminescence,
     Lasing.
We shall in this article focus on the material aspect of
semiconductor optoelectronic device technology. The range
of semiconducting materials that are in current use, to-
gether with the more important physical considerations
behind their choice, will be outlined in order for representa-
tives of each of these four device classes. The discussion
will be simple, aiming at an overall and up-to-date picture,
rather than the details which can be obtained in the
literature selected and cited here.

Photodetectors

     The employment of the photoconductivity effect to detect
radiation is the oldest among these four uses of semiconduc-
tors. Photoconductive selenium was studied in the
'laboratory' in as early as 1873, and it was the principal
material in commercial use until about 25 years ago. The
real progress came when the Germans during the Second World
War used lead sulphide and selenide in their infra-red
detectors, which exceeded a few hundred times in speed and
for the first time also in sensitivity the performance of the
conventional thermoelectric and bolometric devices, until
today the typical semiconductor infra-red detectors are
similarly a few hundred times more sensitive than the
bolometer. Their major drawback is their selectivity in the
wavelengths of light to which they will respond, especially
on the long wavelength side, although in specific applications
this can be an advantage. In either case, the result is the
great number of semiconductors used: besides PbS, PbSe, and
PbTe, included are the II-VI compounds, the III-V's (notably
InSb), Ge, the 'inevitable' Si, and others.
     Figure 1 shows schematically what materials are commonly
utilised over what wavelength ranges. The data are extracted
from the literature as well as specifications of commercial
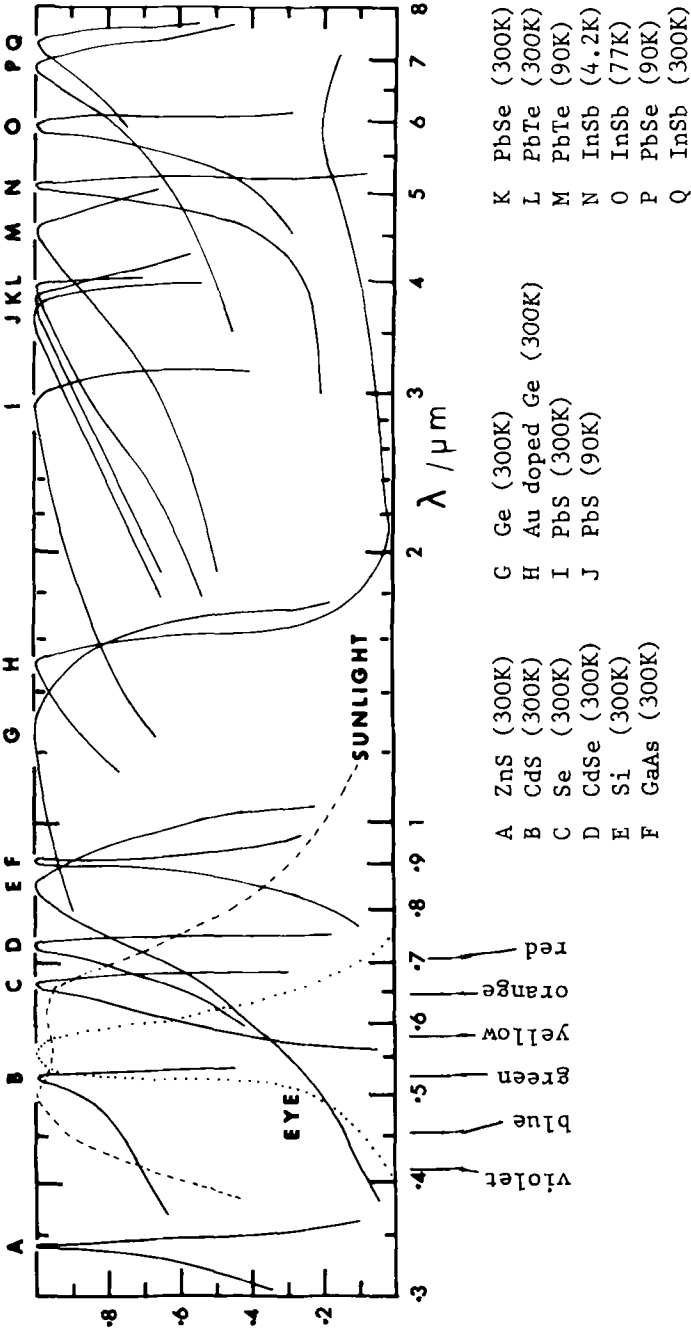products (bulk photoconductors and homojunction photodiodes).

Fig.1.   Semiconductors Normalised Spectral Response (also included are spectra of human vision and sunlight).

It can be seen that the response shifts to longer wavelength
with decreasing temperature, in the case of the lead-salt
compounds; the opposite, however, is usually true of the
other semiconductors. Cases where the operation conditions
are very inconvenient have not been included. Also excluded
are heterojunctions, and alloys such as $Pb_{(1-x)}Sn_xTe$. As one
example, in the laboratory n-type InSb cooled to liquid helium
temperature and in an applied magnetic field of 0.38 tesla is
responsive at the peak out to 26μm (1,2). By varying the
composition the response of an alloy is often 'tunable'
quasi-continuously over a wide wavelength range. Hetero-
diodes, e.g. of PbS-GaAs, can have flat bandpass responses
(3) and fast response times (4). Furthermore, the photo-
voltaic infra-red detector will not be discussed, either
here or in the following section; in any case the range of
materials used for it is not wide, comprising Si, Ge, and some
of the III-V compounds (5).

As photoconductivity depends on the excitation (by light)
of electrons to the conduction band, there is for the
responsivity of any given material a long-wavelength cutoff
limit $λ*$. Incident photons of longer wavelength and therefore
lesser energy (than the band gap or, in the case, of a doped
material at low temperatures, i.e. impurity photoconduct-
ivity, than the gap between the impurity level and the con-
duction/valence band) will no longer increase the charge
carriers concentration. Also, there exists a useful para-
meter, the short-wavelength limit $λ_*$. Near it, the optical
absorption coefficient, which is a function of the incident
light wavelength, becomes so large that near-complete
absorption occurs within a short distance from the surface
of the semiconductor, where the lifetime of the (minority)
carrier is very short. A negligible number of the photo-
generated carriers drifts to the electrodes and contributes
to the current. The semiconductors used in photo-detectors
are $10^{-3} \sim 10^{-2}$cm thick, and the critical value for the
absorption coefficient may representatively be taken as
10^5cm^{-1}. Table 1 lists the room-temperature values of $λ*$,
and $λ_*$ (corresponding to the above value of the absorption
coefficient), for some intrinsic semiconductors.

After the spectral responsivity, other important para-
meters of the material are the charge carrier mobility, the
carrier lifetime $τ$, the (internal) quantum efficiency $η*$,
and others (11). Under a given light intensity the actual

TABLE I

Response limit of intrinsic semiconductors

Material	λ^* μm	λ_* μm	Reference
Amorphous Se	0.67	0.56	6
GaAs	0.92	$\sim$ 0.62	7
Si	1.1	0.39	8
Ge	1.87	0.67	8
PbS	3.1	$\sim$ 0.62	9
PbTe	4.0	$\sim$ 1.03	9
PbSe	4.6	$\sim$ 0.69	9
InSb	7.7	> 0.83	10

response, which obviously should be as high as possible, is
(12) proportional to the product $\mu\tau\eta^*$, while the response
time constant (which is required to be fast) is easily seen
to be proportional to τ. Hence, high μ and η^* are good, but
for τ there is a compromise. Among the commonly used photo-
conductive semiconductors, CdS has the highest η^* (about
10^4), and its response can reach 50 ampere/lumen. CdSe gives
a slightly lower response, but its response time (about 100μs
typically) is faster. However, as a general problem for most
II-VI compounds, this is still comparatively very slow.
Moreover, although their single-crystal growth process has
been known for a long time (13), it remains expensive. Si
has, and in the past Ge had, the most advanced technology
and their μ and τ values are not bad; unfortunately their
η^* never exceed 1. In the spectral region where either can
be used, Si is preferred because if an extremely small series
resistance is required it can be more easily highly doped, as
it has higher impurity solubilities, and it gives a lower
capacitance, as its dielectric constant is lower (11.8
compared to 16). Higher on the wavelength scale, up to 3μm,
PbS is still often used as it was 30 years ago. Its response
time of 10μs or more is not very fast, but the response is
very high. Between 3μm and 5μm, PbTe gives the highest
response, but only if cooled to 90K. Further up, to 7.5μm
at room temperature, but to 5.5μm only at 90K, InSb is
normally used. Its μ is extremely high, and although its

τ even in pure single crystal is on the contrary very small,
infra-red detectors made from it (e.g. Mullard ORP 10) will
respond to objects only a few degrees hotter. Response time
is fast, from 0.1 to 1μs. Besides, after Si and together
with GaAs, it has the most advanced technology. Single
crystals (and not merely thin films) of InSb can be obtained
(14) cheaply. To go deeper still in the infra-red, the
impurity photoconductivity of various types of doped Ge are
used (up to 0.12mm if liquid helium cooling is used).
Although they received attention as early as the 1950's (15),
as yet only a few cases have been exploited commercially.
Certain binary and ternary selenide and telluride compounds
may also be used, but these materials in general still have
many technical problems (11).

We have not considered applications like Si, Ge and GaAs
as infra-red prisms, filters and laser windows, since they
are based on optical but not optoelectronic effects in the
semiconductors. It should be mentioned, however, that based
on the dependence of optical absorption coefficient on charge
carrier concentrations, Si and Ge infra-red modulators (16)
have been produced in as early as 1954. Amorphous Se is
commonly employed in xerography, which is based on the effect
of electrostatic discharge by light ('opto-electrostatics').
In contrast to InSb, its μ is extremely low (in fact, nearly
10^5 times smaller) and it gives low response, but in this
application this is not very important. Its large band gap,
hence higher (dark) resistivity and hence the capacity of
storing charge for a long time is used here to great advan-
tage.

Solar cells

The photovoltaic ('solar') cell was first developed in
1954 at Bell Labs, using a diffused silicon p-n junction.
Since then it has found an important place in space
applications; the 20kW of electrical power for the Skylab
orbiter, for example, is derived solely from its bank of
solar cells (17). Further, in recent years, terrestrial
applications of direct solar energy conversion have
attracted great interest. It is not inconceivable that the
solar cell may constitute the next 'consumer' product 'boom'
after the present pocket-calculator and electronic watch
phenomena!

Many semiconductors have been investigated for possible
use in solar cells besides silicon. In fact, at the same time
the first silicon solar cell was produced, the III-V compounds
were regarded as capable of reaching greater efficiences (18).
Materials that have been used are diffused GaAs (19); thin-
film GaAs (20), CdTe (21), CdS (22), Se-CdS (23), CuO-CdS(23),
Cu_2S-CdS (24), CuS-CdS (24), $CuInSe_2$-CdS (25), InP-CdS (26);
and a few alloys (notably GaAs-$Ga_{(1-x)}Al_xAs$ (27).) There have
been many attempts (17,28,29) to set up realistic models to
calculate the maximum energy-conversion efficiency as a func-
tion of the semiconductor band gap. They give numerically
different values for the efficiencies, but the functional
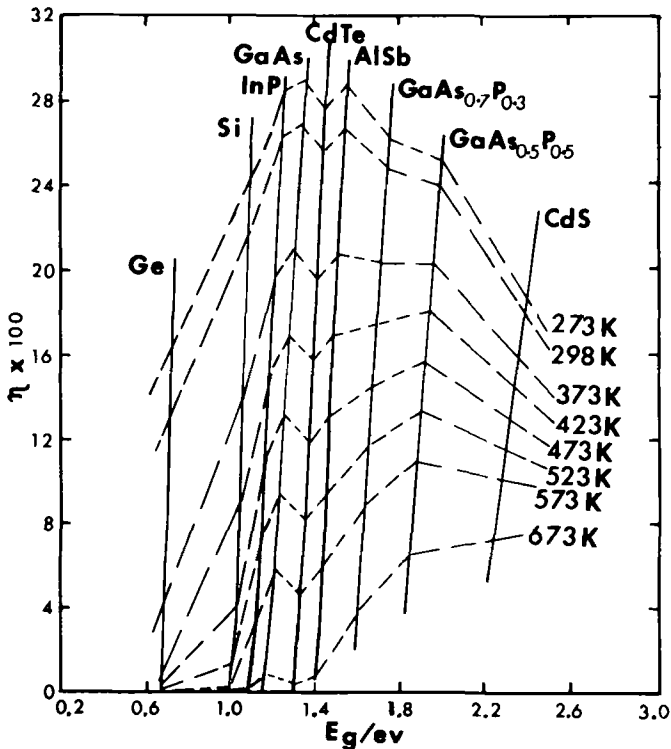dependence have similar shapes. Fig.2 gives a typical result.

Fig.2. Efficiency of solar photovoltaic energy conversion
for different semiconductors at various temperatures,
assuming ideal current-voltage characteristics (after (29)).

It can be seen from Figure 2 that, at room temperature,
GaAs has the optimum band gap. At both lower and higher
temperatures, however, the optimum shifts to larger-band-gap
materials. Nowhere does Si lie near it. (Incidentally, the
efficiency of a state-of-the-art solar cell is 0.16. The
best GaAs cell at present gives the figure 0.18). The
dominance of Si is realised only when we consider other
technological factors, like the relative advancements in
material preparation and fabrication. When a single crystal
is used for a cell the crystal has to be of high purity (to
maintain a low electron-hole recombination rate), which can
be done most easily in Si; in fact, had it not been possible
to use also polycrystalline thin films, most other materials
with the exception of GaAs would not have been used. (The
production of thin films costs much less than that of single
crystals but the efficiencies obtained are lower, and they are
more suitable for terrestrial applications). The Si solar cell
is at present ten times cheaper to produce than a GaAs cell of
similar efficiency. It will without doubt continue to
dominate the market for some years, with latest advance in its
technology like the vapour-phase epitaxial (30) junction
fabrication (31) on large-area ('continuous') ribbons produced
by an edge-defined film-fed process (32).

Light emitting diodes

A p-n junction diode can be made to luminesce by
applying a d.c. forward current; such electroluminescent
diodes are commercially called light emitting diodes (l.e.d.).
For materials used in l.e.d., as in semiconductor lasers, the
most important physical consideration is the band structure.
In these devices, light energy is the output, and high quantum
efficiency (and thus high energy-conversion efficiency) is
obtained only if radiative interband transitions of electrons
predominate over non-radiative processes like Auger recombi-
nations (33). This consideration explains the downfall here
of the 'classical' silicon, in which this is not the case.

The discovery in 1952 of the semiconducting III-V com-
pounds (34) which with the notable exception of GaP satisfy
this condition, can thus be considered the first important
event in the history of the practical exploitation of semi-
conductor electroluminescence. To this day they and their
derivatives remain the basic materials for l.e.d. technology.

For a review on l.e.d. materials and an assessment of the
state-of-the-art in 1971, see (35) and relevant sections in
(40). In the near infra-red region, GaAs is best. Operating
at room temperature and at 20K, a typical GaAs l.e.d. has an
overall (external quantum) efficiency approaching 0.073 and
0.405, light emission peaking at $0.91\mu m$ and $0.84\mu m$, respec-
tively (36). Advancement in its technology like the low-cost
liquid-phase epitaxy (LPE) (37) has already produced the planar
beam-lead l.e.d. array (38).

     In applications where the output is coupled to the human
eye, the band gap   must be in excess of 1.8eV so that the
radiative emission is in the visible region. Only GaP has a
large enough band gap, but on the other hand it gives a low
efficiency of 0.0005 (39). One solution is to go over to the
alloy $GaAs_{1-x}P_x$, which (x = 0.4) gives a red emission at
$0.65\mu m$ (40). Technological considerations like the relative
ease of its vapour-phase epitaxial growth on GaAs substrates
and subsequent p-n junction fabrication by the diffusion of
zinc to produce high efficiency diodes (41) explain its
popularity among l.e.d. manufacturers. Similar considera-
tions, however, rule out any large-scale commercial use of
the alloys $Al_xIn_{(1-x)}P$ and $Ga_xIn_{(1-x)}P$ whose epitaxial growth
is possible (42) but expensive, although their green emission
at 0.53 for x = 0.41 (43) and at $0.55\mu m$ for x = 0.8 to ~ 1 (44)
respectively, fall in the optimum region. (A green l.e.d.
appears to the human eye 10 times brighter than a red one
emitting the same photon flux (40). Another solution is to
introduce isoelectronic substitutes into GaP. Substitution
with zinc-oxygen pairs enhances the red emission,   with
nitrogen the green luminescence.   Nitrogen doped GaP
(GaP:N), grown by LPE (a technique originally developed for
GaAs), produces cheaply the commercial highest-efficiency
(0.006) green l.e.d. (45). High efficiency (0.005) red
emitting diodes are produced from GaP:Zn-O (46). $GaAs_{0.35}$-
$P_{0.65}$:N diodes emit red-orange light with an efficiency of
0.0025 (47). SiC, Zn-doped GaN, and GaAs (Si substitutes)
are used for deep green and blue l.e.d., and high resistive
ZnTe for orange emitting diodes, but a different physical
effect (namely emission via avalanche breakdown with diode
in reverse bias) is involved in the operation.

     From the band structures of the II-VI compounds, which
are more ionic and whose band gaps are therefore larger, we
know that their luminescence is around the visible region;

the quantum efficiency should be high as well. Further,
isoelectronic substitution is possible also for them, e.g.
ZnTe:O (48) and CdS:Te (49). Unfortunately, no commercial
l.e.d. have been made from them: ZnS and other sulphides and
selenides can probably never be made sufficiently strongly
p-type, and ZnTe never usefully n-type, by any doping process
including type conversion by ion-implantation (50), so that
low resistive, sufficiently efficient junctions are un-
obtainable (40,51). (For CdTe the junction has been fabricated
and electroluminescence at an efficiency of 0.12 observed at
77K (60), but its band gap of $\sim$1.5eV is too small for visible
emission). Instead, their visible luminescent potential is
utilised in powder form (sintered or embedded) as 'phosphors'
in image recording panels and in photoanodes of high-speed
image converter cameras, and (conjunctive with photoconduct-
ivity, usually from another material) in solid-state light
intensifiers. ZnS is the most common semiconducting 'catho-
doluminescent' (luminescent by electron bombardment) phosphor;
CdS and CdSe in the case of photoluminescence (light emission
through optical de-excitation, when illuminated). However,
as these applications are not strictly optoelectronic, we
shall not go into detail.

     Recently, a soft ultra-violet l.e.d. made from 'undoped'
GaN, electroluminescence peaking at 0.385μm (52), has been
reported.

Lasers

     Compared with the other classes of (primary) lasers,
semiconductor lasers are more compact in size, faster in
operation, and can be operated with relatively high-
frequency modulation (if incorporated for communication
applications). The major disadvantage is the comparatively
poor coherence of the emission. However, continued advances
in semiconductors technology such as liquid-phase epitaxial
growth (of GaAs and GaP, etc.) and heterojunction fabrication
(notably GaAs-$Al_xGa_{(1-x)}As$) are constantly pushing them to
the front. First achieved for diffused GaAs diodes in 1962
(independently at MIT Lincoln Lab, General Electric and IBM
Yorktown Research Centres), the lasing is obtained by current
injection in a planar p-n junction; alternatively, in one
homogeneous structure, via avalanche breakdown, or by optical
or electron beam excitation (coherent photo- and cathodo-

'luminescence', respectively). The injection type is the most
convenient in operation, due to its frequent compatibilities
with silicon integrated circuits and printed circuitry
(possible because a forward-biased junction has a very low
impedance). Theoretically it also offers the highest energy
conversion efficiency. The three other types, on the other
hand, are useful when lasing junction fabrication is difficult
for the semiconductor concerned.

The most important consideration for a laser is obviously
the wavelength of the emission. Although sometimes this can
be significantly shifted by varying the impurity doping and
operative temperature (as in GaAs), the lengths (in the case
of injection lasers) of the diode and of the external cavity
if present (52), the hydrostatic pressure on the material (54),
the length and intensity of the (electron beam) excitation (55),
or the magnetic field if applied (for small-gap semiconductors
such as InSb), the wavelength is basically determined by the
band structure of the semiconductor used. Table 2 lists the
emission wavelengths of all currently known lasing semiconduc-
tors (56). For completeness the materials for all four types
of lasers are included. We see that broad (quasi-continuous)
tuning of wavelengths is possible for the ternary compounds
by varying their alloy compositions. The lead salts lase in
the infra-red; the III-V compounds just outside the visible.
To go into the visible, we have to use the II-VI compounds
and their derivatives.

However, being amphoteric, the II-VI's as noted before
are difficult materials to make p-n junctions from. (For
CdTe (60) and the hetero-structure CdTe-ZnTe (61) and ZnTe-
ZnSe (62) the junction has been fabricated and quite efficient
electroluminescence observed but lasing conditions cannot be
achieved). Some other excitation methods are employed for
them.

Among the other considerations, the most important one
is the threshold current density (in the case of injection
lasers) below which only incoherent emission but not lasing
will take place. It is in part directly proportional to the
square of the energy band gap of the semiconductor, but it
also depends on the temperature, the diode length, the
reflectivity of the resonator and other factors which cannot
be entirely correlated with the physical parameters of the
material. In Table 3 some measured typical values are given

Table II. Lasing Semiconductors (After (56))

Wavelength (μm)	Material	
0.33	ZnS	
0.358	GaN (57)	
0.37	ZnO	+
0.46	ZnSe	
0.32 − 0.49	$Zn_xCd_{(1-x)}S$	
0.49	CdS	+
0.53	ZnTe	
0.59	GaSe	
0.675	$CdS_{0.05}Se_{0.95}$	
0.49 − 0.675	$CdS_xSe_{(1-x)}$	?
0.675	CdSe	
0.785	CdTe	
0.61 − 0.90	$GaAs_xP_{(1-x)}$	+*
0.63 − 0.90	$Al_xGa_{(1-x)}As$	+*
0.55 − 0.91	$Al_xIn_{(1-x)}P$	*?
0.59 − 0.91	$Ga_xIn_{(1-x)}P$	*?
0.84 − 0.91	GaAs	+*
(depending on temperature and diode length (65))		
0.91	InP	*
1.01	$CdSnP_2$	*
0.9 − 1.55	$GaSb_xAs_{(1-x)}$	*
1.55	GaSb	*
2.1	Cd_3P_2	
1.77	$In_{0.65}Ga_{0.35}As$	*
2.07	$In_{0.75}Ga_{0.25}As$	*
0.85 − 3.1	$In_xGa_{(1-x)}As$	*?
0.942	$InP_{0.06}As_{0.94}$	*
1.6	$InP_{0.49}As_{0.51}$	*
0.9 − 3.2	$InP_xAs_{(1-x)}$	*?
3.1	InAs	*
3.19	$InSb_{0.02}As_{0.98}$	*

Cont.

Table II (Continued from previous page)

Wavelength (μm)	Material	
3.72	Te	
3.8	$Cd_{0.32}Hg_{0.68}Te$	
4.3	PbS	
3.1 - 5.2	$InSb_xAs_{(1-x)}$	*?
5.0 - 5.2 (depending on magnetic field (58))	InSb	*
6.5	PbTe (68)	*
3.9 - 8.5	$PbS_xSe_{(1-x)}$	*
8.5	PbSe (68)	*
3 - 15	$Cd_xHg_{(1-x)}Te$	?
18.8	$Pb_xSn_{(1-x)}Se$ (59)	
9.5 - 28.0	$Pb_xSn_{(1-x)}Te$ (64)	*
28	PbSnTe	*
8 - 34	PbSnSe	*

+ lasing at room temperature reported
* lasing by junction injection possible
? lasing probably but not yet confirmed

as available from the literature. No doubt further advances in junction fabrication technology will lead to lower still values.

Conclusions

In perspective, despite the fact that their markets are directly commercialised (and sometimes militarised), opto-electronic devices as hardware do contribute to one phase of the progress of the society. They are demanded because they are useful and not simply because they can be produced. There still exist many areas where significant improvement in device performance will follow immediately from breakthroughs and developments in materials technology. Current programs in optoelectronic materials research are mainly concerned with

the preparation and fabrication of existing materials and the
characterisation and evaluation of new materials. Theoretical
works such as the analysis of performance dependence on
material parameters are also receiving attention. Continued
efforts in these directions will be fully justified.

Table III. Threshold Current Densities

Threshold current density (Acm^{-2})	Material	Temperature (K)	Reference
7.0 x 10	InP	4.2	63
1.25 x 10^2 $\big\}$	$Pb_{0.73}Sn_{0.27}Te$	$\big\{$ 12.0	64
> 3 x 10^4		77.0	64
1.5 x 10^2	InP	20.0	63
2.5 x 10^2	GaAs	4.2	65
3.0 x 10^2	InAs	4.2	66
6.0 x 10^2	GaAs	77.	65
5.5 x 10 ? $\big\}$	$Pb_{0.83}Sn_{0.17}Te$	$\big\{$ 12.0	64
6.0 x 10^2 ?		12.0	67
6.7 x 10^2	$Pb_{0.86}Sn_{0.14}Se$	12.0	67
9.0 x 10^2	$Al_xGa_{(1-x)}As (x \to o)$	77.	55
1.1 x 10^3	PbTe	12.0	68
1.4 x 10^3	InSb	1.7(longitudinal magnetic field of 3.1 tesla applied)	58
2.0 x 10^3	PbSe	12.0	69
3.0 x 10^3	InAs	77.	66
3.5 x 10^3	$Al_{0.66}Ga_{0.34}As$	77.	55
3.0 x 10^4	$In_{0.65}Ga_{0.35}As$	1.9 $\big\}$ (1.4 tesla applied)	70
3.0 x 10^4	$In_{0.75}Ga_{0.25}As$	1.9	70
5.6 x 10^4	$Al_{0.66}Ga_{0.34}As$	300.	55
6.1 x 10^4	GaAs	300.	65
1.2 x 10^5	$Al_xGa_{(1-x)}As (x \to o)$	300.	55

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